This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

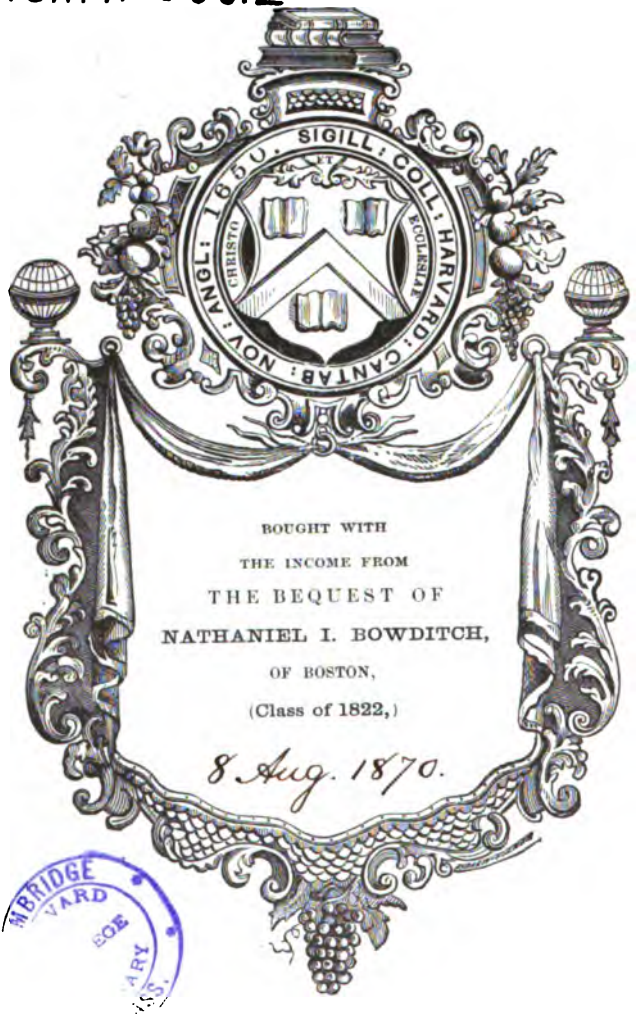
+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

Chem 7108.55.2



MBRIDGE
VARD
EGE
ARY
SS.

SCIENCE CENTER LIBRARY

LIST OF CHEMICAL WORKS

PUBLISHED BY H. BAILLIERE.

Chemical Society (Quarterly Journal of the) 15 vols. 8vo. London, 1848—62. Vols. 1 to 7 have been reduced to 8s. each; Vols. 8 to 15, 13s. each. Or in Quarterly Parts, price 3s. each.

The years 1862-3-4 are published Monthly at 1s. each number.

———— Memoirs and Proceedings of the Chemical Society of London for 1841—1848. 3 vols. 8vo. and Plates. 15s.

Campbell.—A Practical Text Book of Inorganic Chemistry. 12mo. 6s. 6d.

Chapman.—Practical Mineralogy. 8vo with 13 Engravings. 7s.

———— Brief Descriptions of the Characters of Minerals. 12mo. 4s.

Day (G. E.)—Chemistry, in its Relations to Physiology and Medicine. By George E. Day, M.D., late Professor of Medicine in the University of St. Andrews. 8vo. illustrated with 30 Engravings. 1860. £1.

Dumas & Boussingault.—The Chemical and Physiological Balance of Organic Nature: an Essay. 1 vol. 12mo. 4s.

Ganot.—Elementary Treatise on Physics, Experimental and Applied. Translated from the Ninth Original Edition by Dr. Atkinson, M.C.S., Lecturer on Chemistry and Physics, Royal Military College, Sandhurst. With 600 Illustrations. Post 8vo. 1863. 12s. 6d.

Gesner.—A Practical Treatise on Coal, Petroleum, and other Distilled Oils. 8vo. New York, 1861. 7s. 6d.

Graham.—Elements of Chemistry; including the Application of the Science in the Arts. By T. Graham, F.R.S., L. & E., Master of the Mint, late Professor of Chemistry at University College, London. 2nd Edition, revised and enlarged, copiously illustrated with Woodcuts. 2 vols. 8vo. £2.

Isherwood (B. E.) Engineering Precedents for Steam Machinery; embracing the Performances of Steamships, Experiments with Propelling Instruments, Condensers, Boilers, &c., accompanied by Analysis of the same; the whole being original matter, and arranged in the most practical and useful manner for Engineers. 2 vols. 8vo. With a Plate and Tables, New York, 1859. 18s.

———— Experimental Researches in Steam Engineering. By Chief Engineer B. F. Isherwood, U. S. Navy. Vol. I., 4to., with 17 Plates. Philadelphia, 1863. £3 3s. The whole being original matter, composed of Extensive Experiments made by the U. S. Navy Department.

Kæmptz.—A Complete Course of Meteorology. By L. F. Kæmptz, Professor of Physics at the University of Halle. With Notes by Ch Martins, and an Appendix by L. Lalanne. Translated, with Additions, by C. V. Walker. 1 vol. post 8vo. pp. 624, with 15 Plates, cloth boards, 1845. 12s. 6d.

Liebig.—Chemistry and Physics. 8vo. 3s.

Mitchell (J.) Manual of Practical Assaying. For the Use of Metallurgists, Captains of Mines, and Assayers in General. Second Edition, much enlarged, with Illustrations, &c. 8vo. £1 1s.

Moquin-Tandon.—Manual of Medical Zoology: being a Detailed Description of Animals useful in Medicine, and the Species hurtful to Man; with General Considerations on the Organization and Classification of Animals, and with a Resumé of the Natural History of Man. Edited, with Additions, by R. T. Hulme, Esq. With 124 Wood Engravings, post 8vo. 12s. 6d.

Otto.—Manual of the Detection of Poisons by Medico-Chemical Analysis. 12mo. 7s.

Reid.—Rudiments of Chemistry. 12mo. 2s. 6d.

Reichenbach.—Physico-Physiological Researches on the Dynamics of Magnetism, Electricity, Heat, Light, Crystallization, and Chemism. 8vo. Plates. Edited by J. Ashburner, M.D. 1851. 15s.

Regnault.—Elementary Treatise on Crystallography. 8vo. Illustrated by 108 Woodcuts 8s.

Thomson.—Chemistry of Organic Bodies: Vegetables. 8vo. £1 4s.

——— Heat and Electricity. 2nd Edition. 8vo. 15s.

MESSRS. T. PRENTICE AND CO.'S GUN-COTTON FACTORY, STOWMARKET.

LIBRARY

OF

ILLUSTRATED

STANDARD SCIENTIFIC WORKS.

VOL. XV.

RICHARDSON AND WATTS'S

CHEMICAL TECHNOLOGY;

OR,

CHEMISTRY,

APPLIED TO THE ARTS AND TO MANUFACTURES.

VOL. I. PART IV.

LONDON:
HIPPOLYTE BAILLIERE, PUBLISHER,
219, *REGENT STREET.*

1865.

CONTENTS OF THE VOLUMES

ALREADY PUBLISHED.

Chemical Technology; or, Chemistry in its Applications to the Arts and Manufactures.

Vol. I., Parts 1 and 2, 8vo. contain—FUEL and its APPLICATIONS. Profusely Illustrated with 433 Engravings and 4 Plates. 2nd Edition. £1 16s.

Vol. I., Part 3, 8vo. contains—The ACIDS, ALKALIES, and SALTS, their Manufacture and Applications, with Articles on Soap, Potash, Railway Grease, Glycerin, &c. With 367 Illustrations on Wood. 2nd Edition. 1863. £1 13s.

Vol. I., Part 4., 8vo. contains—Aluminium and Sodium, Soda, Phosphorus, Lucifer Matches, Borax, Artificial Mineral Waters, Gunpowder, Gun-cotton, Fireworks, &c. With Illustrations. 1865. 21s.

(*Part 5, containing the Organic Acids and their Salts, in the Press*).

Vol. II., 8vo. contains—GLASS, ALUM, POTTERIES, CEMENTS, GYPSUM, &c. With numerous Illustrations. £1 1s.

Vol. III., 8vo. contains—FOOD GENERALLY, BREAD, CHEESE, TEA, COFFEE, TOBACCO, MILK, SUGAR. With numerous Illustrations and Coloured Plates. £1 2s.

Graham.—Elements of Chemistry; including the Application of the Science in the Arts. By T. GRAHAM. F.R.S., L. & E., Master of the Mint, late Professor of Chemistry at University College, London. 2nd edition, revised and enlarged, copiously illustrated with Woodcuts. 2 vols 8vo. 1850–1857. £2.

Ganot.—Elementary Treatise on Physics, Experimental and Applied. Translated from the Ninth Original Edition by Dr. ATKINSON, M.C.S., Lecturer on Chemistry and Physics, Royal Military College, Sandhurst. With 600 Illustrations. Post 8vo. 1863. 12s. 6d.

CHEMICAL TECHNOLOGY;

OR,

CHEMISTRY IN ITS APPLICATIONS

TO THE

Arts and Manufactures.

BY

THOMAS RICHARDSON, M.A., PH.D., F.R.S.E., M.R.I.A., ASS. INST. C.E., &c.
READER IN CHEMISTRY IN THE UNIVERSITY OF DURHAM;

AND

HENRY WATTS, B.A., F.C.S.,
EDITOR OF THE JOURNAL OF THE CHEMICAL SOCIETY.

Second Edition,
ILLUSTRATED WITH NUMEROUS WOOD ENGRAVINGS.

VOL. I.—PART IV.

ACIDS, ALKALIES, AND SALTS,

THEIR MANUFACTURE AND APPLICATIONS.

LONDON:
H. BAILLIÈRE, PUBLISHER, 219, REGENT STREET.

NEW YORK:
BAILLIÈRE BROTHERS,
440, BROADWAY.

PARIS:
J. B. BAILLIÈRE & FILS,
RUE HAUTEFEUILLE.

MELBOURNE (AUSTRALIA):
F. F. BAILLIÈRE,
COLLINS STREET EAST.

MADRID:
BAILLY BAILLIÈRE,
PLAZA DEL PRINCIPE D'ALFONSO.

1865.

Chem7108.55.2

1870, Aug. 8.
Bowditch Fund.

WILLIAM HENRY COX,
5, GREAT QUEEN STREET, LINCOLN'S INN FIELDS.

PREFACE.

We regret our inability to complete the Second Edition of our First Volume with the present Part. The quantity of new matter at our disposal compels us to publish what still remains, in another Part, in which will be found the Organic Acids and their Salts, together with the Abstracts of Patents, and the Chemical Tables.

The present volume contains a description of the production of various Alkaline Salts of a miscellaneous character, and we have grouped them, as far as possible, in relation to their manufacturing affinities; for example, Silicate of Soda, Artificial Stone, and Stereochromy are grouped together; Chlorate of Potash, Phosphorus and Lucifer Matches form another group; whilst the Nitrates of Soda and Potash, Nitric Acid, Gunpowder, Gun-cotton, and Pyrotechnics form a third group.

In the chapter on Phosphorus, we are indebted to Mr. Albright, of Oldbury, for valuable information on the Manufacture of Amorphous Phosphorus, which we hope will soon be exclusively used in the production of Lucifer Matches. The employment of this form of Phosphorus would at once deliver the workpeople from the terrible scourge to which they are now unfortunately

liable, as well as remove the risk of fire and of poison which accompanies the use of this material in its ordinary state. The use of the Amorphous Phosphorus has been strongly urged by MM. Tardeau and Chevalier in their Reports, and by Dr. Bristowe in the valuable Report for 1862, by Mr. Simon, the Medical Officer of the Privy Council

The chapter on Saltpetre contains full details of the various processes for the conversion of Nitrate of Soda into this Salt. The Patent of Mr. Hill of Deptford, having expired, a great revolution is taking place in this trade; and instead of depending upon India for a supply of this important material, the Potash from the Vinasse, Kelp-liquors, and the Salt beds of Luneburg are now being employed in increasing quantities for the manufacture of Nitrate of Potash.

The chapter on Gunpowder has been greatly extended, and several new patent processes and materials have been fully described. The important experiments of Bunsen and Schischkoff, as well as those of Karolyi on the gases produced by the explosion of Gunpowder, have been given in considerable detail. We are also greatly indebted to the able Chemist of the War Department for much valuable information he has communicated, and for his kindness in revising the proof sheets of this chapter.

We are also enabled, by the kindness of Dr. Gladstone and Mr. J. Scott Russell, to include, in the present volume, a very interesting and valuable account of the chemical history and mechanical effects of Gun-cotton, which has been prepared by these gentlemen. This wonderful material—"the explosive of the future"—promises to acquire an importance superior to that of Gunpowder: its advantages, which will be found fully detailed in the chapters referred to, being, uniformity of composition; greater safety in manufacture; non-liability to

injury from damp; perfect conversion into gases by explosion,—so that it makes no smoke, leaves no residue to foul the gun, and, in mining operations, does not injure the ventilation; and capability of exploding either instantaneously or gradually, according to the kind of work for which it may be used. The researches of Baron Lenk, on this material, have been crowned with such success, that its production has become a regular manufacturing operation, and there is now no difficulty in obtaining it of a uniform composition, however large the scale on which it is made. Through the enterprise of Messrs. T. Prentice and Co., of Stowmarket, it is now an article of English manufacture, and this firm are prepared to supply it in any quantity for military or mining operations.

In the chapter devoted to Fireworks, we have included all the information we could procure connected with this interesting manufacture, and Mr. W. H. Darby, the well-known pyrotechnist of Lambeth, has added much new matter, while kindly revising our proof-sheets.

In conclusion, we have again the pleasure of thanking our Publisher for sparing no expense in illustrations to render the present volume as useful as possible.

THOMAS RICHARDSON,
HENRY WATTS.

January 1, 1865.
NEWCASTLE-UPON-TYNE, AND
LONDON.

CONTENTS.

	PAGE
Aluminium and Sodium	1
Historical Notices	3
Preparation of Sodium	4
Continuous preparation of Sodium in Cylinders ...	8
Preparation of Aluminium on the large scale	10
From Chloride of Aluminium	*ib.*
Preparation of Alumina	*ib.*
From Ammonia-alum	*ib.*
From Cryolite	*ib.*
Preparation of Chloride of Aluminium	12
Ditto of Chloride of Aluminium and Sodium ...	15
Reduction of Aluminium from the Chloride ...	*ib.*
From Cryolite	19
Reduction of Aluminium by Hydrogen, Charcoal, &c. ...	21
Gerhard's Process	*ib.*
Knowle's Process	*ib.*
Corbelli's Process	23
Cumenge's Process	*ib.*
Reduction of Aluminium by Electrolysis	24
Purification of Aluminium	26
Properties of Aluminium	27
Uses of Aluminium	29
Alloys of Aluminium	*ib.*
Amalgamation and Gilding of Aluminium	32
Stannates of Soda and Potash	34
General Notices	*ib.*
Manufacturing Operations	*ib.*
Young's Processes	35
Richardson's Process	42
Haeffely's Process	43
Dale's Process	*ib.*
Valuation of Tin Ores	44
In the dry way	*ib.*
In the wet way	45
Analyses of Tin Ores	46

PAGE

Tungstates of Soda and Potash 47
General Notices ... ... *ib.*
Manufacturing Operations 48
Oxland's Process ... ... *ib.*
Spilsbury's Process 52
Applications of Tungstate of Soda ... ... *ib.*
Valuation of Ores of Tungsten 54
Analyses of Tungsten Ores 55

Chromates of Potash and Soda 57
General Notices 58
Manufacturing Operations 59
Ordinary Process ... ... *ib.*
Tilghmann's Processes 60
Swindell's Process 61
Booth's Process ... ... *ib.*
Jacquelain's Process 63
Adulteration of Bichromate of Potash 64
Preparation and uses of Chromic Acid 65
Valuation of Chrome Ores 66
Analysis of Chrome-iron Ores 68

Silicates of Potash and Soda 69
Historical Notices 70
Preparation of Water-glass 72
Fuchs's Method ... ... *ib.*
Soda Water-glass 73
Double Water-glass ... ... *ib.*
Fixing Water-glass 74
Ransome and Kuhlmann's Processes ... ... *ib.*
Hardinge's Apparatus 75
Properties of Water-glass 77
Composition of Water-glass 78
Uses of Water-glass 79
1. Hardening and Preserving Stones, &c. ... ... *ib.*
Artificial Stone 81
Ransome's Processes ... ... *ib.*
Way and Paine's Process 83
Hardinge's Process 85
Ellis's Process 86
Cementing and Hardening Wood, &c. 88
Hardening and Preserving of Building Stones ... 89
2. Silicious Painting—Stereochromy 94
Fuchs's Method ... ... *ib.*
Colours for Stereochromic Painting 99
Kuhlmann's Method 100

PAGE

Chlorate of Potash... 104
General Notices ... ... *ib.*
Manufacturing Processes 105
Uses of Chlorate of Potash 107
Consumption of Chlorate of Potash 110

Phosphorus ... ... *ib.*
Historical Notices 111
Manufacture of Phosphorus ... ... *ib.*
Purification of Phosphorus 115
Moulding of the Phosphorus 117
New Plans—Mantrand's Process 119
Fleck's Process 122
Gentele's Process 123
Laming's Process 124
Bessemer's Process 125
Statistics of the Trade ... ... *ib.*
Amorphous Phosphorus 126
Historical Notices ... ... *ib.*
Preparation of Amorphous Phosphorus 127
Albright's Process ... ... *ib.*
Uses of Phosphorus 130

Lucifer Matches 131
General Manufacturing Processes 132
Lucifers without Sulphur 135
Vesta Matches ... ... *ib.*
Fusees 136
Matches tipped with Amorphous Phosphorus 137
Paste for ditto 139
Manufacturing Operations 143
Safety Matches, ignited by rubbing against a prepared surface 145
Matches without Phosphorus 146
Gurney and Mill's Safety-Fusees 149
Machinery for Cutting and Dipping Matches 150
Tillett's Machine ... ... *ib.*
Partridge's Machine 153
Zulzer's Machine 154
Bell and Grime's Machine 159
Urion's Machine 162
Cook's Machine 170
Newton's Machine 175
Statistics of the Match Trade 180

Hyposulphite of Soda 183
General Notices ... ... *ib.*
Manufacturing processes 184
Losh's process 185
Applications of Hyposulphite of Soda 186

PAGE

Borax 187
General Notices ... ... *ib.*
Occurrence of Boracic Acid 188
Method of obtaining Boracic Acid 190
The Lagoons ... ... *ib.*
Clarification 191
Evaporation ... ... *ib.*
Crystallization 195
Constituents of the Crude Acid ... ... *ib.*
Statistics of the Trade 197
Valuation 198
Uses of Boracic Acid ... ... *ib.*
Preparation of Borax ... ... *ib.*
Crystallization 201
Sautter's Process 203
Native Borax (Tinkal) ... ... *ib.*
Valuation of Borax 205
Borate of Ammonia 207
Borate of Lime ... ... *ib.*
Composition of ditto 209
Bell and Schofield's Process for Preparation of Boracic Acid from ditto 211
Beatson's Process for the same 212
Richardson's Application of Borate of Lime 213

Soluble Phosphates 215
General Notices 216
Phosphates of Soda, &c. ... ... *ib.*
Phosphates of Lime 217
Phosphates in Cultivated Plants 219
In Bones, Bone Ashes, &c. 221
Manufacture of Superphosphate 226
Valuation of Superphosphate 229
Statistics of the Trade 231
Analysis of Superphosphate 232

Artificial Mineral Waters 233
Historical Notices ... ... *ib.*
Simple Gaseous Water ... ... *ib.*
Manufacture of ditto 234
Apparatus of Savaresse 235
Ditto Ozouf 236
Ditto Gaffard 240
Geneva Apparatus 242
Apparatus of J. Tylor and Sons 245
Receipts for Making Aërated Waters 247
Bottling and Corking of Gaseous Waters ... ... *ib.*
Pitching and Capsulage 250

Artificial Mineral Waters—*Continued.* PAGE

Extemporaneous Manufacture of Gaseous Water ... 251
Fountains for Artificial Waters 255
Apparatus for Uncorking 257
Artificial Mineral Waters, properly so-called 258
General Notices ... ... *ib.*
Manufacture of Artificial Mineral Waters 259
Imitation of Natural ditto 260
Ditto Natural Sulphurous Waters 266

Saltpetre and Nitre 269
General Notices ... ... *ib.*
Sources and Manufacture of Nitrate of Soda 271
Manufacture of Nitrate of Soda from Caliche 273
Statistics of the Trade 275
Nitrate of Potash 276
Occurrence of Native Saltpetre ... ... *ib.*
Formation of Saltpetre in the Temperate Zones ... 279
Saltpetre from Walls 280
Production of Saltpetre in Switzerland ... 281
Ditto ditto at Longpoint ... ... *ib.*
Ditto ditto in Sweden 282
Saltpetre Plantations 283
Theory of the Process of Nitrification 289
1. Direct Oxidation of Nitrogen 291
2. Oxidation of Ammonia 292
3. Oxidation of Organic Compounds 293
Treatment of Ripe Saltpetre-Earth 294
Lixiviation of the Earth ... ... *ib.*
The Crude Lye 298
Treatment of the Lye 299
The boiling 300
Refining Process 304
Production of Nitrate of Potash from Chili Saltpetre ... 310
Newton's Process 311
Gentele's Process 314
Wölner's Process 316
Production of Nitrate of Potash from Ashes of the Beet-root Sugar-works 317
Preparation of Nitrate of Potash from Nitrate of Soda and Chloride of Potassium 318
Use of Baryta-salts in the Preparation of Nitrate of Potash from Nitrate of Soda 322
Cooper's Process for Making Nitrate of Potash with Carbonate of Lead and Sulphate of Soda 323
Testing for Purity, or Refraction of Saltpetre 325
Swedish Process ... ... *ib.*
Riffault's Process ... ... *ib.*
Gay-Lussac's Method 326

Saltpetre and Nitre—*Continued.* PAGE
Husz's Method 327
Gossart and Pelouze's Method 331
Reich's Method 335
Persoz's Method for the complete Analysis of Saltpetre 336

Nitric Acid 337
Historical and General Notices ... ... *ib.*
Theory of its Production 338
Distillation of Nitric Acid in Glass Retorts 340
Ditto in Cast-iron Cylinders 342
Fractionation of the Products 345
Decoloration of the Product ... ... *ib.*
Improved Methods of Condensation 346
Chevé's direct Preparation of Colourless Nitric Acid ... *ib.*
Devers and Plisson's Condensing Apparatus ... 347
Purification of Commercial Nitric Acid 349
Special Modes of Preparation 350
By the Action of Chloride of Manganese on Nitrate of Soda *ib.*
Ditto of certain Sulphates on Alkaline Nitrates ... 351
Ditto of certain Metallic Oxides, &c. on Nitrates ... *ib.*
Preparation of Fuming Nitric Acid 352
Uses of Nitric Acid 353
Detection and Estimation of Nitric Acid... 354
Detection by Means of a Protosalt of Iron ... ... *ib.*
By Formation of Ammonia 355
By the Reaction with Phenyl-Compounds 356
By the Formation of Nitro-prussides 357
By the Decoloration of Indigo ... ... *ib.*
By the Evolution of Chlorine 358
By Ignition with Charcoal Powder ... ... *ib.*
To Distinguish Nitrates from Nitrites ... ... *ib.*
Quantitative Estimation... 360
I. Gravimetric Methods ... ... *ib.*
1. By Neutralization with Baryta ... ... *ib.*
2. By Loss of Weight of Nitrates on Ignition ... 361
3. By Conversion of Nitrates into Sulphates ... 362
4. By Conversion of Nitrates into Chlorides ... *ib.*
5. By the Action of Arsenious Acid 363
Estimation of Water in Nitrates ... ... *ib.*
Separation of Chlorides from Nitrates 364
II. Volumetric Methods ... ... *ib.*
1. By Neutralization with Standard Alkaline Solution ... ... *ib.*
2. By the Oxidation of Protosalts of Iron—Pelouze's Method 365
Schloesing's Method ... ... *ib.*
3. By the Reducing Action of Mercury ... 366
4. By the Reducing Action of Copper at a red-heat. *ib.*

Nitric Acid—*Continued.* PAGE
5. By Conversion into Ammonia 367
Martin's Method ... ... *ib.*
Harcourt's Method 368
6. By Reduction to Binoxide of Nitrogen ... 370

Gunpowder 372
Historical Notices ... ... *ib.*
The Peculiar Action of Gunpowder 377
Products of Decomposition 378
Bunsen and Schischkoff's Methods of Combustion ... 382
Karolyi's Method 384
Analyses of the Products 385
Materials of gunpowder 387
The Saltpetre ... ... *ib.*
The Sulphur 388
The Charcoal ... ... *ib.*
Preparation in Iron Cylinders 389
Carbonization by Superheated Steam 393
Other Modes of Preparation 395
Preparation of the Mixture and further Operations 397
The Pulverizing Drums ... ... *ib.*
Powder Mills with Stampers 399
Ditto with Edge-runners 402
Ditto Willett's Improvements 404
Ditto Waltham Abbey Process 406
Ditto Hall's Improvements 407
Ditto Moistening the Charge 415
Ditto ditto Willett's Plan 416
Condensation of the Powder 418
Granulation, or Corning 419
Ordinary Process 421
Waltham Abbey Process 422
Continental Processes 423
Glazing 427
Drying 430
Packing, &c. ... ... *ib.*
Special Descriptions of Powder 431
Round-grained Powder by the Bernese or Champy Process ... *ib.*
Gunpowder Prepared with Nitrate of Soda 435
Davey's Blasting Powder 436
Lannoy's White Blasting Powder, or *Lithofracteur* ... 437
De Tret's Blasting Powder ... ... *ib.*
Augendre's White Gunpowder ... . *ib.*
Davies and Paine's White Gunpowder 439
Fire-Annihilator—Bucher's ... ... *ib.*
Phillips's ditto 441
Properties of Gunpowder—Outward Appearance 442
Density ... ... *ib.*

Gunpowder—*Continued.* PAGE

Apparent or Gravimetric Density of the Powder ... *ib.*
Apparent Density of the Grain... 443
Real Density of the Grains 445
Magnin's Apparatus ... ... *ib.*
Mallet's Densimeter ... ... *ib.*
Densities of various kinds of Powder 448
Inflammability of Gunpowder 449
Firing of Gunpowder by Electricity 452
By the Voltaic Battery ... ... *ib.*
Statham and Brunton's Contrivance ... 452
With Electro-Magnetic Induction Apparatus ... 454
Verdu's Rheotomic Arrangement ... 455
Savarre's Arrangement 456
Wheatstone and Abel's Experiments ... *ib.*
By Friction-Electricity 458
By Magneto-Electricity 460
Abel's Experiments 461
Abel's Fuzes 462
Savarre's Method 464
Wheatstone's Arrangement 465
Force of Powder 466
Rumford's Estimate 468
Bunsen and Schischkoff's Estimate ... ... *ib.*
Hutton's Estimate 471
Illustrations of the Force of Powder 472
Rock at Round Down ... ... *ib.*
Blasting of the Royal George 473
Methods of Testing the Force of Powder 474
By Testing-Mortars ... ... *ib.*
By Robins's Ballistic Pendulum 475
By Regnier's Method 476
By the Hydrostatic Proof Test 477
By Brettes's Electro-Ballistic Pendulum ... *ib.*
By Havez's ditto ditto ... 479
Analysis of Gunpowder ... ... *ib.*
Determination of Moisture ... ... *ib.*
Ditto of the Nitre ... ... *ib.*
Ditto of the Sulphur and Charcoal ... ... *ib.*
By an Alkaline Monosulphide or Sulphite... ... *ib.*
By Bisulphide of Carbon 480
By Conversion of Sulphur into Sulphuric Acid ... *ib.*
By Nitric Acid and Chlorate of Potash ... *ib.*
By Deflagration with Nitre ... ... *ib.*
By Permanganate of Potash ... ... *ib.*
Statistics 481
Great Britain 482
France ... ... *ib.*

PAGE

Gun-Cotton 483
Historical Notices ... ... *ib.*
Chemical Composition 486
Process of Manufacture 487
Lenk's Precautions ... ... *ib.*
Lenk's Method 488
Messrs. Prentice's Steeping Apparatus 489
Abel's Experiments at Waltham Abbey 491
Preparation of the Cotton 492
Ditto of the Acids 493
Treatment of the Cotton with the Mixed Acids ... *ib.*
Purification of the Gun-cotton 495
Treatment with Soluble Glass 497
Effects of the Mixed Acids previously used ... 499
Properties of Gun-cotton ... ... *ib.*
Alteration of Gun-cotton 500
Messrs. Hall's Gun-cotton buried 16 years 501
Explosive Properties 502
Composition of the Gases ... ... *ib.*
Abel's Experiments on the Combustion of Gun-cotton... 503
Practical Application to Gunnery 505
Forming the Cartridges ... ... *ib.*
Advantages of Gun-cotton 506
Practical Application to other Military Purposes 509
Fuses ... ... *ib.*
Shells 510
For destroying Palisades, Bridges, &c. ... ... *ib.*
Under Water ... ... *ib.*
Application to Blasting ... ... *ib.*
Collodion ... ... *ib.*
Nature of the Gun-cotton used 512
Preparation of Collodion for Photographic Purposes ... 513
The Nitre Process .. .. *ib.*
The Process with Mixed Acids ... ... *ib.*
Collodion for the Dry Process 516
Other Applications of Collodion 517
Mechanical Applications of Gun-cotton 518
Destructive Effect ... ... *ib.*
Mechanical Duty 519
On the Nature of the Mechanical Duty to be performed in Artillery 520
The Mechanical Duty of a Gun 521
How to do this Work 522
How Steam would do this Work 523
How Compressed Air would do the Work ... 524
How Compressed Gases would do the Work ... *ib.*
How Gunpowder and Gun-cotton would do the Work ... ... *ib.*

Gun-cotton—*Continued.* PAGE

On the Measures of the Power of Gun-cotton and Gunpowder 525
Whether Gunpowder or Gun-cotton is the best producer of Gases 526
On the relative strength of Gunpowder and Gun-cotton... 527
On the Manner of using Gun-cotton and Gunpowder for purposes of Artillery 531
How not to burst the Gun ... ... *ib.*
With Gunpowder a different Method is necessary... 532
How to form a Gun-cotton Cartridge ... ... *ib.*
On the Manner of using Gun-cotton for destructive purpurposes 533
How to destroy the Chamber ... ... *ib.*
General Lenk's Discoveries and Experiments 534
On Recoil ... ... *ib.*
Whether Gunpowder or Gun-cotton admits of most rapid firing ... ... *ib.*
What advantages Gun-cotton has in continuous firing and breech-loading 538
On the advantages of Gun-cotton for Forts, Ships and Casemates ... ... *ib.*
On its use in Channels ... ... *ib.*
On its use in Smooth-bore Guns 539
On its use in Rifle Guns 540
On its application to Small Arms 541
On its application to Mines 542
Experiments on blowing up Bridges ... ... *ib.*
Experiment on Explosion under Water 546
Experiments on Engineering Works under Water ... 547
First Experiment: Blowing up a Coffer Dam ... *ib.*
Experiment on Blowing up Ships 549
Experiment on Blowing down a Stockade 550

Pyrotechny—Fireworks 551
Historical Notices ... ... *ib.*
Preparation of the Materials and Apparatus 552
Materials ... ... *ib.*
Zinc ... ... *ib.*
Copper 553
Iron-sand 553
Soda Powder ... ... *ib.*
Lead Powder ... ... *ib.*
Prepared Blood ... ... *ib.*
Apparatus 554
Formers or Rollers ... ... *ib.*
Rolling Table ... ... *ib.*
Rolling Board ... ... *ib.*
Preparation of the Cases 555

Pyrotechny—Fireworks—*Continued.* PAGE

Quick-match 556
Touch-paper 558
Port Fires ... ... *ib.*
Leaders or Pipes of Communication 560
Single Fireworks ... ... *ib.*
Crackers ... ... *ib.*
Revolving Crackers 562
Squibs 563
Serpents (or Marroon Squibs) 567
Gerbes ... ... *ib.*
Iron Case Gerbes 568
Darby's Italian Gerbe ... ... *ib.*
English Pin-wheels 569
Simple Stars or Fireballs 570
Sparks 573
Roman Candles or Fire-pumps 574
Chinese Fire ... ... *ib.*
Gold Rain 575
Marroons ... ... *ib.*
Battery of Marroons ... ... *ib.*
Saucissons 576
Terrestrial Fireworks 577
Suns 578
Mosaics... 579
Palm Tree 580
Water-fall ... ... *ib.*
Pièce Pyrique ... ... *ib.*
Chinese Fountain 582
Fixed Fire-globes ... ... *ib.*
Rolling Fire-globes 583
Fire-wheels ... ... *ib.*
Single Vertical Wheels 584
Double Vertical or Bisecting Wheels 585
Plural Wheels... ... ... *ib.*
Horizontal Wheels 586
Caprice and Furilona Wheels ... ... *ib.*
Spiral Wheels 587
Plate-wheel or Table-piece ... ... *ib*
Balloon Wheels ... ... *ib.*
Pastiles or Pin-wheels 588
Dahlia Pastiles 589
Bengal Lights 590
Theatre Fire ... ... *ib.*
Atmospheric Fireworks 592
Rocket 593
Sky-rockets 594
Moulds and Cases for do. 595
Sticks for do. 596

Pyrotechny—Fireworks—*Continued.* PAGE

Charges for Rockets 597
Towering Rockets 598
Honorary Rockets ... ... *ib.*
Caduceous Rockets... 599
Line Rockets or Courantines ... ... *ib.*
Revolving Courantines or Pigeon Wheels ... 600
Table Rockets ... ... *ib.*
Chained Rockets ... ... *ib.*
Signal Rockets 601
The Peacock's Tail ... ... *ib.*
The Wing Rocket ... ... *ib.*
The Girandole 602
War Rockets ... ... *ib.*
Construction of do. ... ... *ib.*
Rocket Tube 603
The ground Volley 604
Hale's Rockets ... ... *ib.*
Rockets without Rods 605
Scrolls for Rockets ... ... *ib.*
Luminous Rods for Rockets ... ... *ib.*
Parachute Signal Light ... ... *ib.*
Aquatic Fireworks 606
Fire-balls 607
Fire-globes ... ... *ib.*
Floating Suns ... ... *ib.*
Water-mines ... ... *ib.*
Water-fire Fountains 608
Water Rockets ... ... *ib.*
Swans and Ducks ... ... *ib.*
Theoretical and General Notices ... ... *ib.*
Statistics of the Trade 611

CHEMICAL TECHNOLOGY;

OR,

CHEMISTRY APPLIED TO THE ARTS

AND

MANUFACTURES.

ALUMINIUM AND SODIUM.

ALUMINIUM is one of the most abundant of the metals, but never occurs in nature in the free state. In combination with other elements, however, it forms a large number of minerals, some of which make up a very considerable portion of the earth's crust. Felspar, which is a silicate of alumina and potash (the potash being sometimes replaced by soda, and partially by lime or magnesia), occurs abundantly in beds and veins, and occasionally forms entire mountain-masses. The same mineral is also an essential constituent of granite, gneiss, porphyry, and others of the older rocks. Moreover, these double silicates, when exposed to atmospheric influences, undergo complete decomposition, the more soluble alkaline silicate being gradually washed away, and the silicate of alumina being left in the form of *clay*, the different varieties of which are produced by the admixture of other substances, chiefly lime and oxide of iron, in various proportions. The purest white clay, or kaolin, used for the manufacture of porcelain, is produced by the decomposition of granite, as may be seen on Dartmoor in Devonshire, and at St. Austell in Cornwall. The less pure varieties, which constitute the marly

and argillaceous soils, so important in agriculture, are produced by the decomposition of felspathic rocks of later geological periods. Alumina, the oxide of aluminium, occurs crystallized in *corundum*, and its varieties, the *ruby* and *sapphire;* a less pure variety, called *emery*, is much used in the state of powder, on account of its hardness, for grinding and polishing glass and other hard substances. A native subsulphate of alumina occurs in the form of *alunite*, or *alum-stone*, a mineral produced in certain volcanic districts by the joint action of sulphurous acid and oxygen on felspathic rocks; and this native sulphate, or the sulphate obtained by decomposing clay or shale with sulphuric acid, yields, when treated with sulphate of potash or ammonia, the double sulphates of alumina and potash or ammonia, called *Alums*. These double salts are also obtained by roasting the alum shales of Yorkshire, Hurlet, and other localities, and treating the clarified liquors by one of the above-named alkaline sulphates. Aluminium also occurs in nature associated with fluorine, in the scarce mineral, *topaz*, which is a fluoride of aluminium, and in *cryolite*, a fluoride of aluminium and sodium, a very large bed of which exists on the coast of Greenland.

But, notwithstanding the great abundance and variety of the natural compounds of aluminium, and the facility with which many others of its compounds can be obtained artificially, the metal itself was till recently but little known. Davy, soon after he had effected the decomposition of the alkalies by electrolysis, endeavoured to decompose alumina in the same manner, and also by heating it with potassium, but did not obtain the metal by either process. Oersted, who in 1824 discovered the method of preparing anhydrous chloride of aluminium by passing chlorine gas over a heated mixture of alumina and charcoal, attempted to decompose this chloride by means of potassium-amalgam, but did not obtain any definite result. Wöhler, who in 1827 repeated Oersted's experiments, also failed to reduce the aluminium; but, by heating chloride of aluminium with potassium in a covered porcelain crucible, he obtained the metal in the form of a grey powder, which acquired a tin-white lustre under the burnisher; and, in 1845, by passing the vapour of chloride of aluminium over melted potassium, he obtained aluminium in small fused globules, having the colour and lustre of tin.

This last method—sodium being, however, used as the reducing agent instead of potassium—has lately been carried out on an

extensive scale in France by M. H. Sainte-Claire Deville,* with the co-operation of M. Debray, MM. Rousseau (frères), and M. Paul Morin; and these chemists have succeeded in obtaining aluminium in compact masses, capable of being hammered into leaf, drawn into wire, and fabricated into various articles of domestic use or ornament.

Aluminium may also be reduced from cryolite, the native fluoride of aluminium and sodium, by heating that mineral with sodium. This mode of preparation was first tried by Professor H. Rose, of Berlin, and Dr. Percy, and is now carried out on an extensive scale at Amfreville, near Rouen, by Messrs. C. and A. Tissier.†

Attempts have also been made, but with doubtful success, to separate aluminium from its compounds by means of the ordinary reducing agents, hydrogen, charcoal, &c. (see pages 21—23).

Lastly, aluminium may be reduced from the fused chloride or, better, from the double chloride of aluminium and sodium, by electrolysis, as shown, first by Bunsen in 1854, and afterwards by Deville. According to some chemists, it may also be reduced by the electric current from the solutions of some of its salts (see page 25).

Aluminium possesses properties which would make it very useful for many purposes in the arts, if it could be obtained at a moderate price. It is very light, possesses considerable hardness and tenacity, is highly sonorous, takes a high polish, and, when pure, is but little tarnished by exposure to the air, and not at all by sulphuretted hydrogen. Such properties render it highly desirable that the metal should be obtained at a price sufficiently low to make it available for ordinary use. Hitherto this end has been but imperfectly attained, the price of aluminium being at present rather higher than that of silver, weight for weight. Nevertheless, the progress already made is considerable, and there is every reason to hope that greater simplifications may yet be effected in the mode of reduction.

The successful manufacture of aluminium depends in great measure on the cheap production of sodium, which is a much more economical reducing agent than potassium, first, on account

* *De l'Aluminium, ses propriétés, sa fabrication, et ses applications:* par M. H. Sainte-Claire Deville. 8vo. Paris, 1859.

† *L'Aluminium et les Metaux Alcalins*, par MM. Charles et Alexandre Tissier. 12mo. Paris et Rouen, 1858.

of the greater facility with which it is obtained, and, secondly, because its combining number (23) is much lower than that of potassium (39), and consequently, a smaller quantity of it suffices to do a given amount of chemical work.

PREPARATION OF SODIUM.

Sodium and potassium were discovered in 1807 by Sir H. Davy, who obtained them by subjecting the hydrates of soda and potash to the action of a powerful voltaic battery. Soon afterwards, Gay-Lussac and Thénard obtained these metals in larger quantity, by decomposing the alkaline hydrates with iron at a white heat; and, subsequently, Brunner introduced an easier mode of preparation, by decomposing the carbonates of potash and soda with charcoal. The mixture is introduced into a large iron bottle, such as those in which mercury is imported, and heated in an air-furnace. The potassium or sodium is then set free, in the form of vapour, and passes through an iron tube fitted into the mouth of the bottle, into a copper receiver surrounded with ice and containing rock-oil. The metal then condenses and collects in drops under the oil. The details of the process will be found in any of the larger Manuals of Chemistry (see "Graham's Elements," 2nd edit. vol. i, p. 521; or "Gmelin's Handbook," Cavendish Soc. Ed. vol. iii, p. 5).

This process, though much easier and more productive than that of Gay-Lussac and Thénard, is, nevertheless, attended with peculiar difficulties, especially in the case of potassium; for a considerable quantity of the potassium vapour unites with the carbonic oxide evolved at the same time, and forms a black solid substance, the so-called carboxide of potassium, which often stops up the connecting-tube, and can only be removed by thrusting in an iron rod; and when this is done, the sudden removal of the obstruction often occasions the forcible projection of the hot contents of the iron bottle; moreover, the black substance is dangerously explosive. To prevent its formation, the entire length of the connecting-tube must be kept at a red heat from beginning to end of the operation. But in that case it is found that, if the large receivers invented by Brunner are used, the whole of the metal escapes in the form of vapour, not a particle condensing in the receiver. For this reason, Maresca and Donny, who made the preparation of potassium the object of minute investigation,

were led to use much smaller receivers, having the form of rectangular boxes, 12 centimeters long, 6 wide, and 4 deep. With such receivers, the condensation of the metal is easily effected.

The preparation of sodium does not present so many difficulties as that of potassium; but to ensure its production in the most economical manner, particular attention is required to three points, viz., the composition of the mixture, the regulation of the heat, and the form of the condensers. The following is the description of the process given by Deville:—

The carbonate of soda is prepared by calcining the crystallized neutral carbonate, $NaO.CO^2+10$ Aq.* It must be thoroughly dried, then pounded, and mixed with a slight excess of pounded charcoal or coal. An inactive substance, viz., pounded chalk, is also added to keep the mixture in a pasty condition during the operation. For preparation on the laboratory scale, the mixture is composed of—

Dry carbonate of soda	717 parts
Charcoal	175 „
Chalk	108 „

For manufacturing operations, the materials used are—

Dry carbonate of soda	30 kilogrammes
Coal	13 „
Chalk	3 „

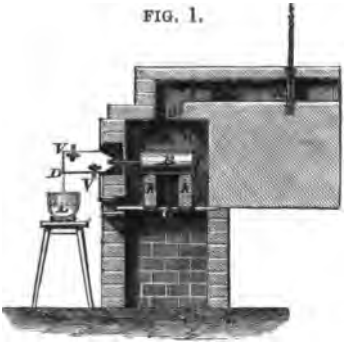
The materials are pounded and sifted, then mixed by the hand and sifted again, so as to ensure very intimate mixture. The mixture, when made, should be used as soon as possible, that it may not absorb moisture.

It is advantageous to calcine the mixture before introducing it into the distilling apparatus, provided the calcination can be effected by means of the waste heat of a furnace; it is thereby rendered more compact, and a much larger quantity can be introduced into a vessel of given size.

* According to Deville, the dry carbonate of soda must be prepared by calcining the crystallized carbonate (*cristaux de soude*), the coarser material, salt of soda (*sel de soude*), obtained by evaporation and direct calcination of the lyes in the manufacture of commercial soda, not being so well adapted for the purpose, because the mixture made with it fuses and obstructs the disengagement of gas. MM. Tissier, on the contrary, state that the common soda may be used quite as well as the calcined crystals, and that the fusion may be completely prevented by properly adjusting the proportions of soda and carbonaceous matter. They also state that the admixture of chalk may be dispensed with.

The distillation is performed either in a mercury bottle or in iron cylinders of large dimensions. The mercury bottle is heated in a furnace (Fig. 1), exactly similar to that which is generally used for the preparation of potassium. Into the mouth of the bottle is screwed an iron tube *T*, made of gun-barrel, and to the other end of this tube is adapted the receiver *V V*, in which the sodium is condensed. The construction of this receiver is a point of great importance; indeed, the success of the preparation appears to be mainly dependent on it.

FIG. 1.



The form of receiver which Deville finds most advantageous is that used by Maresca and Donny for the preparation of potassium. These receivers are made of two plates of iron, from $\frac{1}{12}$ to $\frac{1}{8}$ of an inch thick (2 or 3 millimeters). One of them *A* is turned up at the edges, while the other *A'* is left flat, except at the end *C*, where both plates are formed into a cylindrical neck, an inch (25 millimeters) in internal diameter. The conical portion, which joins the cylindrical neck to the flat body of the receiver, should be made as short as possible. The two portions, when joined, form a rectangular box with a cylindrical neck. Fig. 3 represents a section of the receiver, made by a plane passing through the axis of the neck and perpendicular to the surface of the plates.

FIG. 2.

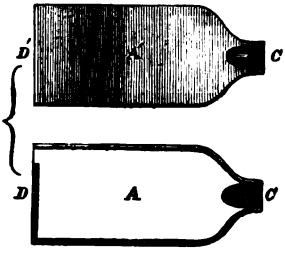
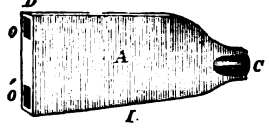


FIG. 3.

FIG. 4.

FIG. 5.



These receivers are either left completely open at the back (Fig. 4), or they may be closed at the back with the exception of a small aperture near the top. With the former arrangement, the condensed sodium flows continuously from the receiver; with the latter it is left to accumulate till the receiver is full. The best

form would perhaps be that shown in Fig. 5, the lower surface being slightly inclined, so as to allow the sodium to run out through the lower aperture *O'*, while the uncondensable gases escape by the upper aperture *O*. The two plates of the receiver are firmly held together by clamps.

The bottle being completely filled with the mixture, the connecting-tube *T* is adjusted, and the bottle is placed in the furnace, resting on the supports *K K*, the furnace having previously been partly filled with lighted coke. It is then filled up with fresh coke, and the register *H* is opened. A considerable quantity of yellow gas is evolved at the beginning of the process. This is allowed to escape, the receiver not being adapted to the tube till a cold iron rod thrust into the bottle comes out covered with particles of sodium, which take fire on contact with the air. When the furnace draws well, and the sodium is quickly produced, the receivers become hot enough to retain the sodium in the liquid state; it then runs out at the open end *D*, and is received in an iron basin *L* containing rock oil. The basin should have a cover to be put on in case the rock oil takes fire. When a closed receiver is used, it is left in its place till quite full, and is then replaced by another.

When the process goes on well, the sodium thus obtained is perfectly pure, the carbonized products, which give so much trouble in the preparation of potassium, being produced in very small quantity only, if at all. Nevertheless, a quantity of somewhat impure sodium always remains attached to the inner surface of the receivers; hence, when a receiver has been used, the plates should be separated and scraped before they are used again; and the matter scraped off, being received under rock oil, may be collected after a while, and will yield by distillation a considerable quantity of sodium. Lastly, the pure metal obtained by this and by the first distillation, is melted under a thin layer of rock oil, which is decanted as soon as the sodium becomes perfectly fluid, and the metal is then run into moulds like those used for casting lead or zinc.

The temperature absolutely required for the reduction of sodium is not much higher than that for the reduction of zinc; but the distillation goes on better, and a larger product is obtained when the temperature is raised considerably higher; according to MM. Tissier, the best temperature is about the melting point of magnetic oxide of iron. It varies, however,

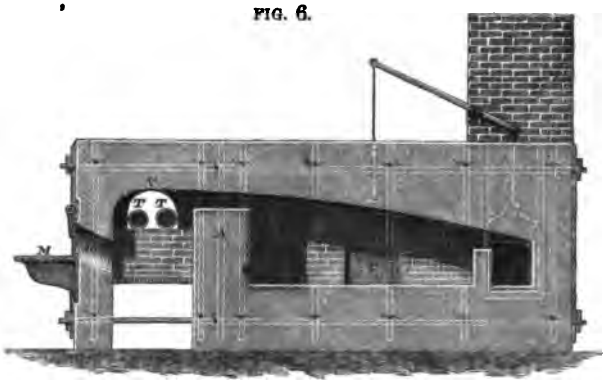
with the quality of the carbonate of soda and the composition of the mixture. The mercury bottles do not require any protecting envelope.

Continuous Preparation of Sodium in Cylinders.—For larger operations, the mixture is heated in iron cylinders so arranged that, at the end of the distillation, the exhausted charge may be withdrawn, and a fresh charge introduced, without displacing the cylinders or putting out the fire. The cylinders, made of wrought iron, are about 4 feet long, 5½ inches in internal diameter, and half an inch thick. They are open at one end *O* (Fig. 7), and closed at the other end *P*, excepting that this extremity is pierced with a circular aperture, to which an iron tube *L* is adapted, having a conical termination for connection with a receiver of the form already described. The open end *O* is fitted with a wrought iron cap terminating in a hook.

A cheaper form of cylinder may be made by rolling up a piece of sheet iron and rivetting the edges. The tube thus formed is closed at the ends with cast iron caps, that to which the receiver is to be adapted being pierced to admit the connecting-tube. These tubes must be made long enough to project beyond the walls of the furnace; otherwise the cast iron caps will be melted.

The iron cylinders, being of less thickness than the mercury bottles, must be protected from the action of the fire by coating them with fire-clay, and enclosing them in tubes of refractory earthenware.

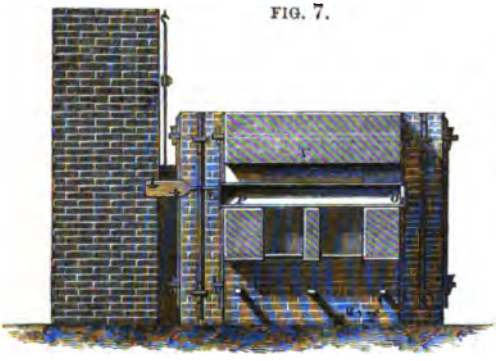
FIG. 6.



The cylinders are heated in a reverberatory furnace (Figs. 6, 7), the fire-place of which is divided into two equal parts by a wall of fire-brick 18 inches high, on which the middle of the cylinders

rests. The fuel is introduced through an aperture *K*, and heaped on a shelf *M*, so as to close the aperture while the process is going on. A wall *A*, reaching a little above the cylinders, keeps the flame in a vertical direction, and the low arch *V* causes it to circulate round the cylinders.

FIG. 7.



The cylinders may also be arranged side by side on the hearth of the furnace, resting on a low wall which runs down the middle. By this arrangement also the flame is made to circulate round the cylinders and heat them uniformly; it likewise affords the means of heating a greater number of them at the same time.

The reduction of the sodium in cylinders takes place in exactly the same manner as in the mercury bottles. The mixture, previously calcined, is introduced in bags of paper or canvas, and the tube is closed with the cap, which is secured with a luting of fire-clay. When the distillation is finished, the cap is detached by throwing a little water upon it, and the residue of the charge, which is a spongy mass of lime and charcoal, mixed with caustic soda and a small quantity of undecomposed carbonate, is withdrawn, and washed with water to extract the alkali. A fresh charge is then introduced; the cylinder is again closed; and, as soon as the flame of sodium appears, the receiver is adjusted, and the distillation continued. In this manner, the process may be carried on without interruption. The mixture should always be calcined before distillation; otherwise, when the fresh charge is introduced into the hot cylinder, the sudden heating of the mixture occasions the projection of a considerable quantity of soda-dust, very unpleasant to the workmen.

The receivers used in these larger operations are of the same dimensions as those which are employed for distillation on the smaller scale (p. 6); large receivers do not condense the sodium so well.

PREPARATION OF ALUMINIUM ON THE LARGE SCALE.

A. *From Chloride of Aluminium.*

This process involves three distinct operations:

1. The preparation of pure alumina.

2. The conversion of the alumina into chloride of aluminium, or the double chloride of aluminium and sodium.

3. The reduction of the simple or double chloride by means of sodium.

1. *Preparation of Alumina.*—In the manufacture of aluminium, it is of the greatest importance to start with alumina as free as possible from foreign substances, especially iron; in fact, it is much easier to get rid of the impurities in this stage of the process than to eliminate them afterwards from the reduced metal.

Alumina may be prepared: *a*, From ammonia-alum or from the commercial sulphate of alumina: *b*. From fluoride of aluminium, as it exists either in cryolite, or in the slag obtained in a process of reduction to be hereafter described.

a. Ammonia-alum or sulphate of alumina is calcined in large iron pots, which may be heated on the hearth of the sodium furnace (Fig. 6, p. 8). The residue of the operation is anhydrous alumina, amounting to about $\frac{1}{9}$ of the weight of the ammonia-alum, or $\frac{1}{7}$ of the sulphate of alumina. It is, however, by no means pure; for the last portions of sulphuric acid adhere very obstinately to it, and the iron, though it may form but a very small proportion of the original salt, being all left in the residual alumina, necessarily exists in that residue in a much larger proportion. Potash also is almost always present. To remove these impurities, the alumina, after being pulverized and passed through a fine sieve, is mixed with a strong solution of caustic soda (45° Baumé) and evaporated. The aluminate of soda thus produced is dissolved in a large quantity of water; the iron is precipitated from it by sulphuretted hydrogen; and the solution, after being left to stand in a close vessel till it has become clear, is subjected, while yet warm, to the action of a stream of carbonic acid gas, which converts the soda into carbonate, and precipitates the alumina in the form of a very dense hydrate, which is washed by decantation, and finally calcined.

b. Cryolite, Al^2F^3. 3NaF, is finely pulverized and mixed

with rather more than $\frac{3}{4}$ of its weight of pure quicklime; the lime is carefully slaked by the addition of a small quantity of water; a larger quantity of water is then added; and the mixture heated by a current of steam. The cryolite is then completely decomposed and converted into fluoride of calcium and aluminate of soda:

$$Al^2F^3.\ 3NaF + 6CaO = Al^2O^3.\ 3NaO + 6CaF.$$

The fluoride of calcium, being very heavy, is easily separated by decantation, and the pure solution of aluminate of soda is decomposed by carbonic acid, as above. Part of the alumina is very apt to combine with the lime, forming an insoluble aluminate of lime, which, however, is easily decomposed by digestion with solution of carbonate of soda. This process yields very good alumina, and also very pure carbonate of soda, which may be used for the preparation of sodium.

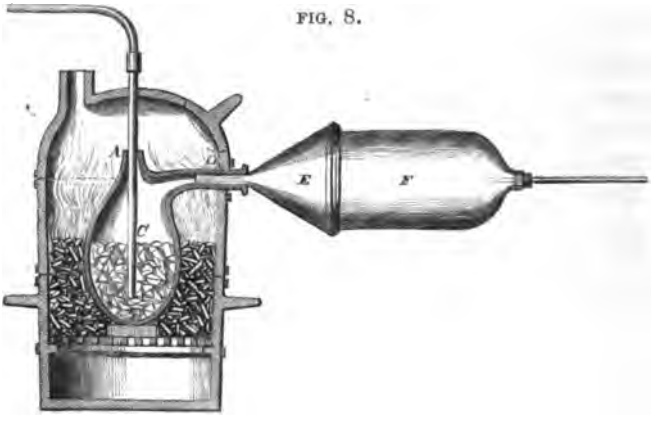
Cryolite is used, as already mentioned, for the direct preparation of aluminium, and also as a flux in the reduction of aluminium from the chloride (p. 17). For these purposes, it should be quite free from iron. Now, the mineral, as imported from Greenland, contains many fragments more or less coloured by carbonate of iron. These should be carefully picked out, only the purest portion of the mineral being reserved for the reduction process, and the ferruginous fragments being used for the preparation of alumina as just described. The iron, for the most part, remains with the insoluble fluoride of calcium. If, however, the proportion of iron is considerable, a small portion of it may pass into the solution of aluminate of soda, and thence into the precipitated alumina. Carbonate of iron is, indeed, decomposed by lime, and yields protoxide of iron, which is slightly soluble in caustic soda.

When cryolite or fluor-spar is used as a flux in the reduction of aluminium from the chloride, as will be hereafter described, a slag is produced, containing 40 per cent. of insoluble matter, consisting of fluoride of aluminium mixed with small quantities of alumina and unaltered fluor-spar or cryolite, the remaining 60 per cent. being chloride of sodium or chloride of calcium, easily removed by washing with water. This slag, together with the residues of the sodium-process, which contain 8·3 per cent. of caustic soda and 14·5 per cent. of carbonate of soda, may be used for the preparation of alumina in the manner just described. 5 or 6 parts of the sodium-residue are carefully

mixed with 1 part of the insoluble portion of the aluminium-slag, the mixture is heated to redness, and the cooled product treated with water. Aluminate of soda then dissolves, and the solution, decomposed by carbonic acid, yields carbonate of soda and a precipitate of alumina. 1,000 parts of sodium-residue and 160 parts of washed slag, yield 110 parts of calcined alumina and 225 parts of dry carbonate of soda. This is a very economical way of using up the waste products.

2. *Preparation of Chloride of Aluminium.*—When alumina is dissolved in hydrochloric acid and the solution is evaporated at a gentle heat, hydrochlorate of alumina, Al^2O^6. 3HCl, or hydrated chloride of aluminium, Al^2Cl^3. 3HO, is left behind. But, on exposing this compound to a higher temperature, hydrochloric acid escapes and alumina remains. Hence it is not possible to obtain the anhydrous chloride of aluminium by simply heating the hydrated chloride. The anhydrous chloride is prepared, as already mentioned, by heating a mixture of alumina and charcoal in an atmosphere of chlorine.

FIG. 8.

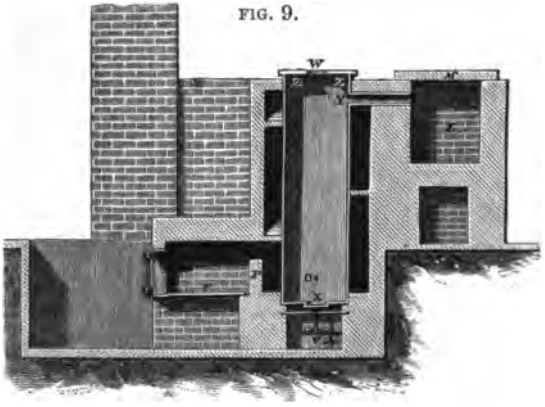


To prepare this anhydrous chloride on a comparatively small scale, the alumina is mixed with 40 per cent. of its weight of pounded charcoal and a small quantity of oil; and the paste thus formed is calcined at a bright red heat. The compact mass thus produced is broken up and introduced into an earthen retort (Fig. 8), placed in a suitable furnace, where it is decomposed by a current of dry chlorine gas conveyed to the bottom by a bent tube *C* passing through the neck of the retort at *A*. At the beginning of the operation, a considerable quantity of water escapes;

but, when this ceases and vapours of chloride of aluminium begin to appear, a porcelain funnel *E* is inserted into the beak of the retort, and to this is adapted a glass bell-jar *F*, in which the whole of the chloride of aluminium condenses as a coherent crystalline mass.

For preparation on the large scale, the alumina is mixed to a pasty consistence with coal-tar, and the mixture is heated in iron pots placed on the hearth of a reverberatory furnace (the sodium furnace). As soon as the fumes of tar cease to escape, the black mass, which is hard, shining, and as porous as pumice-stone, is broken up and introduced while hot into an iron cylinder (a gas-retort), set vertically in a furnace (Fig. 9) and heated by a fire *F*,

FIG. 9.



the flame of which is directed below it by the low wall *P*, and made to circulate round it by a spiral flue *K*. At the bottom of the cylinder is a square aperture 8 inches wide, which is closed by a tile held in its place by a screw *V*. The chlorine is introduced through an aperture *O*, so placed as to be at about the middle of the layer of alumina and charcoal. This mixture is introduced through an aperture *W* at the top of the cylinder, which is afterwards closed with a tile. The cylinder is connected by a tube leading from its upper part, with a condensing chamber *L*, which is of rectangular form, about 4 feet in length and breadth, and 4 feet 6 inches high, lined with plates of glazed earthenware. The cover *M* is movable and formed of one or more plates of glazed earthenware. This chamber is connected at its lower part by means of wooden pipes lined with lead, with a chimney having a good draught. These tubes are provided with dampers, so that

the communication between the chamber and the chimney may be opened and closed at pleasure.

Before beginning the process, the whole apparatus must be thoroughly dried, especially the condensing chamber. This is effected by introducing into it a pan of red-hot coals and keeping it there as long as the walls exhale any moisture. The retort is then slowly heated, the aperture *Z* being left open till it is dry. The mixture of alumina and charcoal is then introduced, the heat raised to redness, and the stream of dry chlorine passed through the mixture. The upper opening is not closed till the vapours of chloride of aluminium appear in large quantities. When the depth of the layer of mixture in the cylinder amounts to about 12 inches, the lower aperture *X* is opened and the exhausted portions are allowed to fall through. Fresh material is then introduced at the top, a sufficient quantity being always kept in the cylinder to cover the aperture by which the chlorine enters; otherwise the sides of the cylinder are attacked. As this accident is likely to occur, even when every precaution is taken, loose bricks should be left here and there in the walls of the furnace, so that it may be examined from time to time. The cylinder should also be so fixed that it may be easily removed when required. An escape of chloride of aluminium is indicated by a blue flame.

When the process goes on well, the chloride of aluminium attaches itself to the upper plate of the condensing chamber, in the form of a solid, coherent, crystalline mass. The carbonic oxide which escapes is free from white vapours, but has a pungent odour, arising from traces of chloride of silicon or chloride of carbon.

Chloride of aluminium is also produced by passing dry hydrochloric acid gas over a very strongly heated mixture of alumina and charcoal.

Chloride of aluminium is of a pale greenish yellow colour, and in considerable masses has a coarsely laminated, crystalline structure; it is semi-transparent and has a waxy lustre. It fumes strongly in the air, giving off hydrochloric acid, and is highly deliquescent. It dissolves in water, alchohol, and ether, with considerable rise of temperature. It sublimes at a moderate heat without previous fusion.

As it is very difficult to keep without decomposition, the quantity prepared at one operation should not be greater than is wanted for immediate use.

Chloride of Aluminium and Sodium.—Al^2Cl^3. 3NaCl.—This double salt, which is now used for the preparation of aluminium, in preference to the simple chloride of aluminium, may be obtained by leading the vapour of chloride of aluminium into a heated chamber containing common salt; but it is better to introduce the chloride of sodium into the mixture of alumina and charcoal in the retort (Fig. 9). As, however, the temperature required for its volatilization is higher than for the simple chloride, the iron cylinder is best replaced by a smaller vessel of earthenware. The condensing chamber *L* may also be replaced by a conical earthen vessel, in which the double chloride condenses in the liquid form.

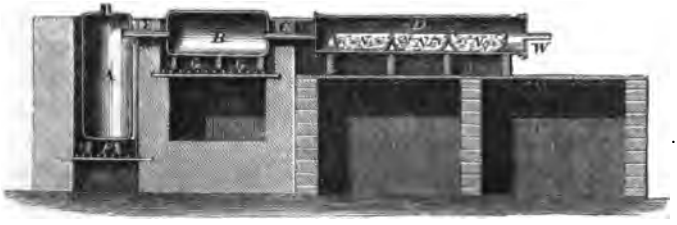
Chloride of aluminium and sodium melts at 200° C. (392° F.) and crystallizes on cooling. When pure, it is perfectly colourless; but a small quantity of iron gives it a yellow colour. It is very permanent in compact masses, and is much less volatile than the simple chloride, being perfectly fixed at ordinary temperatures.

To obtain either the simple or the double chloride in the pure state, it is best, as already observed, to use pure alumina. Nevertheless, when very large quantities are to be prepared, less pure materials may be used, such as pipe-clay or porcelain-clay, or, in short, any substance containing alumina. If the substance used contains too much iron, it must be freed from the greater portion of that metal by calcining it with carbonaceous matter, so as to reduce the iron to the metallic state, and then dissolving it out with a dilute acid.

A patent for the preparation of chloride of aluminium and sodium, as above described, was taken out by MM. Rousseau (21st April, 1856).

Reduction of Aluminium from the Chloride.—The process first adopted by Deville was as follows:—Chloride of aluminium, prepared in the manner just described, was placed in an upright iron cylinder *A* (Fig. 10), heated by a small fire, and distilled

FIG. 10.



into a second cylinder *B*, placed horizontally over another fire, and containing small pieces of iron (*pointes de fer*) by which the sesquichloride of iron in the chloride of aluminium was reduced to the less volatile protochloride. The metallic iron also decomposed any chloride of sulphur or silicon that might be present. From this cylinder, the chloride of aluminium passed on through a wide copper tube *C*, kept at a temperature not exceeding 300° C. so as to retain the protochloride of iron, into a horizontal cylinder *D* of iron or copper, in which were placed three basins, also of iron or copper, each containing 500 grammes of sodium. This cylinder was heated to dull redness, at which temperature the reduction went on at a moderately quick rate. The chloride of sodium resulting from the action united with a portion of the chloride of aluminium, and the resulting double chloride volatilized from the first basin into the second, and from the second to the third. When the decomposition was complete, the basins were removed and left to cool, and the contents were melted in a crucible, whereby any remaining portions of sodium were made to act on the excess of chloride of aluminium present. After cooling, the upper portion of the melted mass, consisting of nearly pure chloride of sodium, was removed; the lower portion containing globules of the metal, was treated with water, and the metallic globules were made to unite by heating them till they began to melt, and pressing them together with a pipe-stem; the whole then united into a single mass, which was remelted and cast into bars. It was by this process that the specimens of aluminium at the French Industrial Exhibition of 1855 were prepared. The process, however, was defective in many points, and the metal which it yielded was impure, containing a considerable quantity of copper, derived from the copper tube and basins in which the reduction took place. This impurity greatly impairs the malleability and ductility of aluminium, and renders it very liable to tarnish.

Another mode of preparation, not yet perfected, but promising to yield very good results, is to reduce the chloride of aluminium by vapour of sodium. The mixture of carbonic oxide and vapour of sodium, produced by heating a mixture of charcoal and carbonate of soda (p. 7), is conveyed into a large earthen crucible, by means of an iron tube passing through a hole near the bottom, and reaching nearly to the other side; and as the sodium and carbonic oxide burn, and thereby heat the crucible, portions of chloride of aluminium are thrown in from time to time. When

the operation is completed, the crucible is broken; the saline mass is disintegrated by digestion in water, acidulated if necessary with a little nitric acid; and the globules of aluminium are united into a mass by fusion, as above.

But the quantity of compact aluminium obtained from the chloride by these processes is considerably below the theoretical amount, a large portion of the metal being reduced in the form of a fine powder, which refuses to unite into globules. Much better results are obtained by adding to the mixture either fluor-spar or cryolite, these bodies assisting the union of the particles, apparently, by dissolving small quantities of alumina—produced by moisture adhering to the chloride—which surround the particles of metal at the moment of reduction, and, not being decomposed by the sodium, prevent them from uniting into globules. The process was first tried as follows:—

400 grammes of chloride of aluminium and sodium, 200 grammes of chloride of sodium, 200 grammes of fluor-spar or, better, of cryolite, all perfectly dry and finely pulverized, were placed, together with 75 or 80 grammes of sodium, in alternate layers in an earthen crucible, which was then moderately heated till the action began, and afterwards to redness, the melted mass being stirred with an iron rod and afterwards poured out. 20 grammes of aluminium were thus obtained in a compact mass, and 5 grammes in globules encrusted with a grey slag.

The aluminium thus obtained was, however, somewhat contaminated with silicon, as the earthy matter of the crucible was attacked by the sodium, by the aluminium, and even by the slag, which contained fluorides. This evil may be corrected to a certain extent, but not completely, by lining the crucible with a paste composed of calcined alumina and aluminate of lime. When cast-iron crucibles were used, the aluminium was found to contain iron.

The reduction is now performed with greater facility, and on a much larger scale, by heating the mixture on the hearth of a reverberatory furnace, at about the temperature required for the reduction of sodium. The proportions used are—

Chloride of aluminium and sodium . .	10 parts
Fluor-spar or cryolite	5 „
Sodium	2 „

The double chloride and the cryolite or fluor-spar are mixed in

the state of powder with sodium in small ingots, and the whole is thrown on the hearth of the furnace previously raised to the required temperature. The dampers are then closed, so as to prevent the access of air as much as possible. A vivid reaction soon takes place, accompanied with so great a rise of temperature, that the walls of the furnace and the mixture itself are raised to a bright red heat, and the mixture is almost completely liquefied. It is necessary, however, to open the dampers, in order to direct the flame upon the hearth in such a manner as to heat the whole mass equally. When the reduction is complete, the fused mass is run out through an aperture at the back of the furnace, and at last the aluminium flows out in a single jet, and collects at the bottom of the liquid slag in one mass. With a furnace having a hearth a square metre or about 16 square feet in surface, the mass thus obtained at one operation weighs from 6 to 8 kilogrammes. The slag consists of two layers, the upper containing a large quantity of common salt, while the lower, which is less fusible and pasty, and of a grey colour, is chiefly fluoride of aluminium. On pulverizing this latter, and passing it through a sieve, an additional quantity of aluminium is obtained in small globules. The slag may be used for the preparation of alumina (p. 11).

The process just described has been patented in England in the name of W. E. Newton (1856, July 1st, No. 1810). It is peculiarly advantageous in this respect, that the reduced metal is very little exposed to contamination with silicon. The introduction of this impurity generally arises from the action of the sodium, or of the slag, on the earthy matter of the crucibles or other vessels in which the reduction takes place. Now, when crucibles are used and the heat is applied from below, the part of the mixture in contact with the crucible is necessarily the hottest, and consequently the action exerted on the crucible is very considerable; but when the mixture is fused on the hearth of a reverberatory furnace, with the flame playing over its surface, the coolest part is in contact with the hearth, and therefore less able to act upon it. Moreover, with the proportions above given, the whole of the fluorine in the slag is in the form of fluoride of aluminium, a compound which exerts but little action on siliceous substances. When aluminium is reduced from cryolite by the action of sodium, as will be presently described, the slag consists wholly of fluoride of sodium, a compound which decomposes siliceous substances with great energy.

A peculiar method of effecting the reduction of aluminium by means of sodium, either from the double chloride or from cryolite, has been patented by F. W. Gerhard (1858, No. 2247). To prevent loss of sodium by ignition, the mixture is covered with a layer of fused chloride of sodium, or of a mixture of this substance and cryolite, or of the slag or scoria resulting after aluminium has been extracted. The reduction is performed in a reverberatory furnace having two hearths, one above the other, or in two reverberatory furnaces or crucibles, one higher than the other, which communicate by means of an iron pipe or discharging passage. In the lower furnace or crucible is placed the mixed compound which is to be treated for the production of aluminium, and in the upper furnace the chloride of sodium or other material which is to form the covering for the mixed compound in the lower furnace or crucible. The latter is then run into the heated lower furnace or crucible, in such quantity that it will completely cover the substance placed therein, the furnace or crucible being kept at the proper heat until the contents are melted; and the mixture is then well stirred and drawn off. After the extraction of aluminium from cryolite, the residuum consists of fluoride and chloride of sodium (the latter having been added as a flux). The chloride of sodium is first removed, and then the fluoride of sodium is pounded and boiled with milk of lime until it is decomposed, after which the caustic soda is separated from the fluoride of calcium, and treated in the usual way for recovering the sodium.

B. *Preparation of Aluminium from Cryolite.*

The pulverized cryolite is mixed with half its weight of common salt, and the mixture is placed, in alternate layers with sodium, in an earthern or iron crucible, the uppermost layer being composed of pure cryolite, and the whole covered with common salt. Two parts of sodium are used for every 5 parts of of cryolite. The mixture is rapidly heated to complete fusion, and the mass is left to cool after being stirred with an earthen rod. The temperature at which the reduction takes place is higher than that required for the decomposition of the double chloride. On breaking the crucible, the aluminium is generally found united in large globules. Such is the method originally given by Professor Rose and Dr. Percy. In the manufacturing process now carried on at Amfreville, near Rouen, by MM. C. & A.

Tissier, the cryolite and sodium are arranged as above in large crucibles of refractory clay, and the melted aluminium is poured, together with the slag, into cast-iron vessels, at the bottom of which it collects in masses. It is then remelted and cast into bars.

According to Rose, the quantity of aluminium obtained by this method is but small, not exceeding $\frac{1}{20}$ of the weight of the cryolite, whereas the quantity actually contained in the mineral amounts to about 16 per cent. or nearly $\frac{1}{6}$. MM. Tissier appear to obtain better results; but the published description of their process is very short, and does not enter into numerical details.

The aluminium obtained from cryolite is generally contaminated with silicon, if the reduction has been performed in earthen crucibles, because the fluoride of sodium produced in the decomposition acts energetically on all siliceous substances. A sample of commercial aluminium, thus prepared, was found by Demondesir to contain 4·4 per cent. of silicon, and 0·8 per cent. of iron. Rose uses iron crucibles, but these generally introduce a considerable quantity of iron into the product. Perhaps the best mode of avoiding the introduction of these impurities, would be to fuse the mixture on the hearth of a reverbatory furnace, as in the method described at page 18; but even then the fluoride of sodium would act more energetically than the fluoride of aluminium produced in Deville's process.

The chief inducemnet for using cryolite as a source of aluminium is, that it is a natural product, obtained with tolerable facility, and enables the manufacturer to dispense with the troublesome and costly preparation of the chloride of aluminium and sodium. Deville is, however, of opinion that the process, as a branch of industry, could never be safely founded on cryolite alone, on account of the uncertainty of supply, the mineral being found only in one locality, viz. at Evigtok, in Greenland; and the vein, though large, being difficult of access, and capable of being worked only for a short time every year. He, therefore, recommends its use only as a flux in the reduction of aluminium from the double chloride, and even for that purpose it may, if necessary, be replaced by fluor-spar. Nevertheless, the supply of cryolite, though not inexhaustible, is at present abundant, and appears likely to continue so for many years; there can therefore be no valid objection to its use, provided only that the process can be so conducted as to yield a pure and abundant product.

C. *Reduction of Aluminium by Hydrogen, Charcoal, &c.*

The following processes have been patented for obtaining aluminium by means of the ordinary reducing agents, without the use of sodium :—

1. *Gerhard's process* (patented 1856, December 16, No. 2980). —Fluoride of aluminium, or the double fluoride of aluminium and potassium or sodium, is decomposed by hydrogen at a red heat, and if the hydrofluoric acid thereby produced is removed as fast as it forms, the aluminium is obtained in the metallic state. The process is conducted as follows:—A number of shallow dishes of well-glazed earthenware, some containing fluoride of aluminium, or one of the double fluorides, and the rest being filled with iron filings, are placed in an oven previously heated nearly to redness. Each dish containing the aluminium compound is surrounded on all sides by dishes containing iron filings. The oven is then carefully closed and heated; the heat increased to redness; and a stream of dry hydrogen introduced through a tube provided with a stopcock; another tube placed at the opposite side of the furnace, and provided with stopcock and safety-valve, allows the gas to escape when the pressure becomes too great. The operation is continued for an hour. The hydrogen unites with the fluorine, forming hydrofluoric acid, which is immediately taken up by the iron, forming fluoride of iron; while the aluminium remains in the metallic state at the bottom of the trays containing the fluoride. When the double fluorides are used, a slag of fluoride of sodium or potassium is of course left behind together with the metal.

This method, when patented, was said to be easy of execution, and to yield good results; but, as the patentee has since returned to the use of sodium (see page 19), it may be presumed that the reduction by hydrogen has not quite answered his expectations.

2. *Sir F. C. Knowles's process* (patented 1857, June 22nd, No. 1742) consists in reducing aluminium from the chloride by means of *cyanide of potassium* or *cyanide of sodium*. It is thus described :—

"To form the cyanides, I combine anhydrous carbonate of potash, or anhydrous carbonate of soda, as the case may be, with fine charcoal in such a proportion as to convert the carbonic acid

into carbonic oxide by the action of heat, and to decompose the alkali used. I place this mixture in a chamber with lumps of charcoal, such chamber being of fire-clay, fire-brick, or iron, and then, having heated the same sufficiently, I pass through it a current of the waste gases of blast furnaces used in smelting iron ores (or of the same or similar gases obtained intentionally from a cupola by a blast of air). The nitrogen contained in these gases combines with the charcoal to form cyanogen, and this, uniting with the metallic base of the decomposed alkali, forms a vapour of the cyanide required, which can be collected by sublimation in appropriate chambers, and cooled.

"To make the metal aluminium, I take one or other of the above cyanides, and the chloride of aluminium, and by passing the vapour of the chloride of aluminium through, or otherwise combining the same in the form of melted chloride, or its vapour, with the melted cyanides, or their vapour, I obtain by double decomposition, chloride of sodium or chloride of potassium, and the metal aluminium, which can be readily collected and fused.

"Pure alumina may be added to the materials to increase the yield of metal, and to economize the cyanide; and this I recommend to be done in most cases.

"The proportions in which these elements decompose each other, and unite in fresh combinations, may be taken as about the following (assuming chloride of aluminium to consist of 2 equivalents of aluminium, and 3 equivalents of chlorine, as at present received):—

"1 equivalent of chloride of aluminium, or 158 lbs.,

"3 equivalents of cyanide of sodium = 148 lbs., or of potassium = 196 lbs., to which may be added, in order to increase the quantity of the metal obtained, and to use up the cyanide completely and economically,

"4 equivalents of alumina = 206 lbs., or generally (to meet the doubt as to the exact chemical composition of the chloride of aluminium),

"3 equivalents of chloride of aluminium,

"39 equivalents of cyanide of sodium or potassium, and

"49 equivalents of alumina will be an equally convenient form, such equivalents in numbers being taken from the best chemical tables in use."

3. *Corbelli's process* (patented 1858, January 26th, No. 142).—L. F. Corbelli, of Florence, prepares aluminium by treating clay, well washed and dried, with strong sulphuric acid or very strong hydrochloric acid, evaporating the liquid to dryness, heating the residue to 450° or 500° C., then mixing it with about twice its weight of dry ferrocyanide of potassium and 1½ times its weight of common salt, and heating the mixture to whiteness in a crucible. After cooling, metallic aluminium is said to be found at the bottom of the crucible. The metal thus obtained must, however, be very impure, and in all probability consists, in great part, of iron.

4. *Cumenge's process* (patented in the name of J. H. Johnson, 1858, March 6th, No. 461).—The object of this invention is to obtain aluminium from the sulphide $Al^2 S^3$, either by removing the sulphur in the form of sulphurous acid or of sulphuretted hydrogen, or by causing it to unite with another metal.

To prepare the sulphide of aluminium, a clay retort, similar to those used in gasworks, is filled to one-half of its length with charcoal or coke, and the other half with alumina, a small orifice being left at each end of the retort. The retort is now heated to redness, and a quantity of sulphur necessary to carry on the reaction is introduced therein through the orifice at the charcoal end of the retort, the gases which are generated passing off by the orifice at the opposite end of the retort. The sulphur becomes volatilized, and in its passage over the incandescent charcoal is transformed into bisulphide of carbon, which passes over the heated aluminium. The carbon takes up the oxygen and forms carbonic oxide gas, whilst the sulphur unites with the metallic aluminium. The sulphide of aluminium thus produced may be treated by either of the following processes:—

First, by reaction in a reverberatory furnace in an unoxidizing atmosphere by mixing it with a sufficient quantity of dry sulphate of alumina or alumina itself, to cause the oxygen of the sulphate or of the oxide added, to be equal to that necessary for oxidizing the sulphur of the sulphide to the state of sulphurous acid. The aluminium remains in a metallic state, and any metal with which it is to be alloyed may now be added.

Second, by reduction with the aid of hydrogen, which expels all the sulphur from the sulphide in the form of sulphuretted hydrogen. The hydrogen may be produced in any well-known

manner, but the most economical mode appears to be the action of steam on incandescent charcoal.

Lastly, the reduction by any of the known metals, iron, copper, zinc, &c., may be effected in the furnaces and after the manner already practised for other metals.

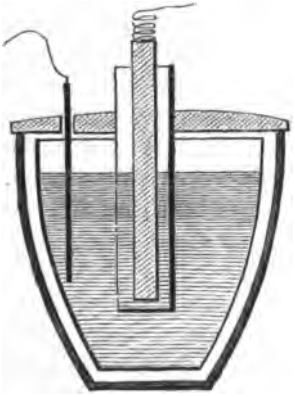
Good metallic alloys may be obtained by the action of aluminium or of sulphate of alumina on the natural or artificial sulphides of other metals, with or without the mixture of charcoal.

D. *Reduction of Aluminium by Electrolysis.*

Aluminium may be reduced by electrolysis from its chloride or other compounds either in the fused state or in aqueous solution. The following is Deville's method of obtaining it from the fused chloride of aluminium and sodium.

The apparatus consists of a glazed porcelain crucible (Fig. 11), enclosed for protection within a common earthen crucible, the whole being surmounted by the cover of the larger crucible, which is pierced with a slit near the side for the introduction of a broad thick platinum plate, forming the negative pole, and with a circular central aperture, through which there passes a well-dried porous tube, containing a cylinder of gas-carbon, for the positive pole. The bottom of the porous tube or cylinder must be kept about an inch above the bottom of the porcelain crucible. The crucible and the porous cylinder are filled to the same height with fused chloride of aluminium and sodium, which is kept in the melted state by heating the crucible over a lamp. On introducing the electrodes and passing the current, the aluminium is deposited on the platinum plate, together with chloride of sodium, while chlorine and a small quantity of vapour of chloride of aluminium escape at the positive pole. A battery of two Bunsen's cells is sufficient for the decomposition. The platinum plate must be taken out from time to time, and the deposit scraped off. This product is afterwards melted in a porcelain crucible, the fused mass boiled with water, to remove chlo-

FIG. 11.



ride of sodium, and the globules of metal remelted. The first portions of metal obtained are generally impure, containing silicon; but afterwards a pure product is obtained, provided the double chloride has been carefully prepared.

The same apparatus may be used for coating metals with aluminium; thus, if a piece of copper be introduced as the negative electrode, and a bar of aluminium as the positive, the latter dissolves as the action goes on, and the aluminium is deposited upon the copper. To obtain a good result, the double chloride forming the bath must be very pure; it is best, therefore, to purify it by passing the current through it for some time before introducing the metal to be coated.

With regard to the electrolysis of aqueous solutions of aluminium-salts, Deville says that all his endeavours to obtain the metal in this manner have given negative results. Mr. Gore, however, appears to have obtained a deposit of aluminium on copper by electrotyping a solution of hydrochlorate and of acetate of alumina, and more slowly from a saturated solution of common alum; and Messrs. Evans & Tilley have patented a process for coating metals with aluminium and its alloys in this manner (1855, December 6th, No. 2756). A solution of alumina, mixed with cyanide of potassium, is submitted to the action of a battery of six Bunsen's or ten Smee's cells, the negative pole being formed of the metal to be plated, while the positive pole is formed, either of platinum or of aluminium, or of some other metal, such as copper, tin, or silver, which is to be deposited together with the aluminium. If, for instance, a plate of copper is to be coated with an alloy of aluminium and tin, the positive pole is formed of a bar of tin, and the waste of aluminium is supplied by adding from time to time a solution of a salt of that metal; or the positive pole may be formed of platinum, and the bath composed of a mixed solution of aluminium and tin salts.

The reduction of aluminium by electrolysis in the wet way has also been patented by L. F. Corbelli (1858, March 12th, No. 507), whose process is so contrived as to yield subchloride of mercury as a secondary product. The solution employed consists of—

Rock alum	5,931 parts, and
Chloride of calcium . . .	2,066 parts;
Or rock alum	5,931 parts, and
Chloride of sodium . . .	2,190 parts;
Or sulphate of alumina .	4,167 parts, and
Chloride of calcium . . .	2,076 parts.

Other salts of alumina base may also be used.

One of these mixtures, well dried and pulverized, is to be placed in a suitable receptacle, which must not be made of metal, and to it must be added about two and a half times its weight of water, in which it is to be dissolved and allowed to settle. The liquid is then to be filtered and placed in a vessel composed of a material which is a non-conductor of electricity, and, a quantity of mercury in the fluid state having been placed in the vessel, a weak current of electricity is to be passed through the mercury and the filtered liquid, for which purpose an insulated iron wire is introduced into the vessel, and brought into contact with the mercury at the bottom of the vessel. This iron wire is brought into communication with the positive pole of a galvanic battery, the negative pole of which communicates with a plate of zinc immersed in the filtered liquid, but suspended so as not to touch the mercury. A galvanic action being now set up, the salts of alumina will be decomposed, and the aluminium will be deposited upon the zinc plate, either in the form of a blackish powder, or in a thin compact sheet. During this operation, the chlorine will be set at liberty, and will combine with the mercury, forming sub-chloride of mercury (calomel), which will be found deposited on the surface of the mercury.

PURIFICATION OF ALUMINIUM.

From *copper* and *iron*, aluminium may be purified by fusion with nitre, the foreign metal being thereby oxidized, while the aluminium remains intact. The operation must be performed in iron crucibles, the inner surface of which has been well oxidized by the action of the nitre itself. Earthen crucibles are quite unfit for the purpose, because the silicic acid which they contain is dissolved by the potash of the nitre, and the glass thus formed is decomposed by the aluminium, which then becomes contaminated with silicon. No method has yet been discovered of purifying aluminium from *silicon*. Aluminium containing *zinc* may be freed from that metal by melting the alloy in contact with the air: the zinc then volatilizes and burns, and the aluminium remains behind.

Aluminium is very apt to retain a portion of the slag in the midst of which it has been formed, its low specific gravity not allowing it to separate easily from the slag. It is very import-

ant to free the metal from this impurity; otherwise, when it is worked and polished, its surface exhibits a number of little points which are less bright than the general surface, and after some time become more conspicuous. The simplest way of effecting the purification is to melt 5 or 6 pounds of aluminium in an open black-lead crucible, keeping the red-hot metal in contact with the air for a considerable time. Acid fumes then escape, arising from the decomposition of the saline matter by the air or by moisture. The crucible is then removed from the fire, and the melted mass is stirred with a cast-iron skimmer, the surface of which has not been freed from oxide. By this means, the whitish slaggy matter is removed, together with a small portion of the aluminium, which is set aside to be re-melted. The metal is then cast into bars, and the entire operation repeated three or four times. (Deville.)

PROPERTIES OF ALUMINIUM.

Aluminium is a white metal with a faint tinge of blue; it takes a fine polish, and its surface may be frosted, like that of silver, by plunging it, for an instant, into a very weak solution of caustic soda, washing with a large quantity of water, and then digesting it in strong nitric acid. When pure, it is quite destitute of taste and odour. It is very malleable and ductile, may be beaten and rolled as easily as gold and silver, and drawn out into extremely fine wire. In this last operation, however, it becomes very brittle, and requires to be tempered by cautious heating over a lamp. In elasticity and tenacity it is about equal to silver. After fusion, it is as soft as pure silver; but after hammering in the cold, it acquires the hardness of soft iron. It is highly sonorous, a bar of the metal suspended by a thread and struck with a hard body emitting a beautiful clear ringing sound. It is very light, being not much more than 2½ times as heavy as water and about 4 times lighter than silver. Its density after fusion is 2·56, and after being hammered in the cold, 2·67. Its melting point is intermediate between the melting points of zinc and silver, but nearer to the former. It may be cast with the greatest ease in metallic moulds, and still better in moulds of sand. It may be melted without any flux—indeed, the addition of a flux is rather detrimental than otherwise, the metal attacking borax and glass with facility. Though its melting point is comparatively low, it takes

a long time to liquefy completely, on account of its great specific heat. When a number of small pieces of aluminium, such as cuttings or turnings, are to be melted into a mass, the crucible must be shaken or the pieces pressed together with an iron rod, the surface of which should not be clean, otherwise an alloy of the two metals will be formed. Aluminium heated in a close vessel does not exhibit the slightest tendency to volatilize.

The electric conducting power of aluminium is 8 times as great as that of iron, and about equal to that of silver; it conducts heat even better than silver; its specific heat is very great. When slowly cooled from fusion, it exhibits a crystalline structure; the crystallization is, however, most distinct when the metal is impure. Aluminium precipitated from its solutions by electrolysis at low temperatures, crystallizes in octohedrons, which appear to be regular. It is slightly magnetic.

Aluminium does not oxidize in the air, even at a strong red heat; neither does it, in the compact state at least, decompose water, excepting at a white heat, and even then but slowly. It is not attacked by sulphuretted hydrogen, or even by sulphide of ammonium, and consequently preserves its lustre in the atmosphere of large towns, where silver is very soon tarnished and blackened. It may also be heated to redness in vapour of sulphur without showing any disposition to combine; at very high temperatures, however, combination takes place.

Aluminium is not attacked by nitric acid, either dilute or concentrated, at ordinary temperatures, and very slowly even at the boiling heat; neither is it acted upon by sulphuric acid diluted to the degree at which that acid dissolves zinc; but hydrochloric acid, either dilute or concentrated, dissolves it readily, even at low temperatures, with evolution of hydrogen. The vegetable acids, such as acetic and tartaric acid, exert no perceptible action on aluminium; a mixture of acetic acid and common salt exerts a somewhat greater action, because it contains free hydrochloric acid; but even in this case, the action is very slow, and not nearly so great as would be exerted upon tin under similar circumstances. Aluminium would therefore be well adapted for culinary vessels, especially as the small quantity of alumina which might be formed from it by the action of certain acid mixtures would not exert any deleterious effect on the animal economy. The hydrates of potash and soda in the state of fusion do not act upon aluminium, but their aqueous solutions dissolve it readily, forming

aluminate of potash or soda, and giving off hydrogen. Ammonia acts but slightly on it.

A solution of common salt or chloride of potassium is also without action on aluminium, but the solutions of many other chlorides dissolve it, and the more readily as the metals which they contain are higher in the scale; even a solution of chloride of aluminium dissolves the metal, forming a basic chloride. Solutions of sulphates and nitrates, on the contrary, do not act upon it. Hence, in precipitating other metals upon aluminium by electrolytic action, it is necessary to use acid solutions not containing hydrochloric acid or any chloride. In an acid solution of sulphate of copper, the aluminium quickly becomes coated with metallic copper.

Aluminium may be fused with nitre at a moderate heat, without undergoing the slightest alteration; hence this process may be adopted for purifying aluminium from admixtures of other metals (p. 26). If, however, the heat be raised till the nitric acid is completely decomposed and begins to give off nitrogen, a new re-action takes place, attended with incandescence, and aluminate of potash is produced.

Uses of Aluminium.—The lustre and whiteness of aluminium and its unalterability in the air when pure, render it well adapted for jewellery, and it is much used for that purpose at present in Paris. The facility with which it takes a frosted surface, by a process already described, is also greatly in its favour in this respect. It also makes very bright reflectors. Its lightness renders it a useful metal for the mounting of telescopes and other astronomical instruments, especially of sextants. It is also an excellent material for small weights, such as the smaller divisions of the gramme. A weight of five centigrammes may be made in aluminium in the form of a cylinder terminated with a knob. A delicate balance has also been constructed of it. For culinary vessels it is well adapted by its lightness, and the little tendency which it has to become corroded by any of the liquids likely to come in contact with it.

ALLOYS OF ALUMINIUM.

Aluminium forms alloys with most other metals. With *zinc* and *tin* it unites readily, forming brittle alloys; with *cadmium* it

yields a malleable alloy. A small proportion of *silver* completely destroys the malleability of aluminium: nevertheless, an alloy containing 3 per cent. of silver has been used for casting ornamental articles, and an alloy containing 5 per cent. for knife-blades. With *iron*, aluminium unites in all proportions, forming alloys which are brittle and hard, and crystallizes in long needles when the proportion of iron amounts to 7 or 8 per cent. Aluminium containing iron dissolves in acids more readily than the pure metal.

The alloys of aluminium and copper are of especial importance. One in particular, containing 10 per cent. of aluminium with 90 per cent. of copper, called *aluminium-bronze*, possesses very remarkable properties. It is a definite compound, containing Cu^9Al. It is of the colour of gold, takes a high polish, is extremely hard, and possesses a tenacity nearly equal to that of the best steel; it is also very malleable. Another alloy containing 2 or 3 per cent. of copper, is used for casting ornamental articles of large dimensions intended to be chased. Aluminium may be easily plated on copper. The plates of the two metals are prepared in the usual manner and well rubbed with sand, then placed between two plates of iron, the whole well bound together, heated to low redness, and then strongly pressed. (Deville.)

Alloys of aluminium may be prepared by reducing a mixture of alumina and the oxide of the other metal with carbon, or by heating a mixture of alumina, carbon, and the other metal. The process has been patented in this country in the name of E. L. Benzon (1858, Dec. 1st, No. 2753).

"To prepare an alloy of copper and aluminium, suboxide of copper (Cu^2O), or protoxide of copper (CuO), or granulated metallic copper, is mixed with alumina and carbonaceous matter, animal charcoal being the best adapted for the purpose. All these ingredients must be as finely divided and intimately mixed as possible, and they must also be combined according to equivalent or atomic proportions.

"It is found desirable to use a little more carbon than is atomically required for reducing the alumina, or if oxides of copper are used, a little more carbon must be added than is required for reducing both oxides (namely, the oxide of copper and the oxide of aluminium). The mixture is put into a melting-pot or crucible, such as those used in melting cast steel, and the bottom

and walls of the pot should be lined or covered with carbon, in order to prevent as far as possible any impurities in the material of which the crucible or pot is composed from affecting the alloy; and after the mixture has been covered with carbon, it must be exposed to a high red heat, say, somewhere about the melting heat of copper, until the alumina is reduced to the metallic state. The heat may then be increased for about half an hour or an hour, in order to melt down the mixture of the metals to an uniform alloy. By this means a series of alloys may be produced, the hardness, ductility, and colour of which will depend upon the per centage of aluminium contained in them. The proportion of copper or the oxides of copper or of the alumina is immaterial (provided the materials be combined according to chemical equivalents), as copper and carbon under the above-named circumstances will always reduce an equivalent proportion of alumina to the metallic state. If, however, it be desired to produce alloys containing certain definite per centages of the metals, copper or any or both of its oxides may be mixed with alumina in the proportion required—of course, basing the calculation on the chemical equivalent of the several ingredients, and an excess of carbon added to ensure the decomposition or reduction of the oxides of the metals. In order to guard against errors arising from imperfectly conducting the process of decomposing the alumina, it is sometimes found convenient in the first place to decompose with the electro-positive metal as large a per centage of alumina as can be conveniently done. The alloy thereby produced is then to be assayed or analysed in order to ascertain the exact proportion of aluminium contained therein; after which, the required quantity of copper or electro-positive metal can be readily added, in order to reduce the alloy to exactly the desired proportion of the two metals.

"The same process as that adopted with copper and its oxides may also be employed to reduce alumina with iron and its oxides. The process is carried on under the same conditions as those above set forth, with the difference only, that a larger excess of carbon must be used, and a higher heat employed and kept up for a longer period than when an alloy of copper is to be produced. The reduction of alumina in contact with the oxides of iron (hammer-slag, for instance), is easier than with pure or metallic iron.

"Either of the above alloys of copper or iron may be mixed with other alloys or metals; for instance, the copper alloy may be mixed

with brass or German silver; zinc or spelter may also be melted down with the copper alloy and another alloy thereby produced. Alumina may also be reduced with copper in the presence of zinc or spelter, and a bronze alloy thereby produced. The iron alloy, produced in the manner above described, may be mixed with steel in the melting-pot, or the alumina may be reduced in the melting-pot with the steel by adding a suitable quantity of alumina with an equivalent quantity of carbon, the added ingredients being in a pulverized or finely divided state, and intimately mixed together."

Some of the alloys thus produced, such as the alloy of iron and aluminium, may be subsequently decomposed, and the pure metallic aluminium obtained separate from the other metal, and used for any of the purposes for which aluminium is employed. The alloy of copper with aluminium possesses the properties already described (page 30). The alloys of aluminium with zinc and copper produce a bronze of beautiful colour and great hardness. The alloy of aluminium and iron will perhaps be found useful for many mechanical purposes, especially in the manufacture of cast steel.

Amalgamation and Gilding of Aluminium.—According to Cailletet, aluminium may be amalgamated by the action of ammonium-amalgam or sodium-amalgam and water; also when it is connected with the negative pole of the voltaic battery and dipped into mercury moistened with acidulated water, or into nitrate of mercury.

Ch. Tissier (Compt. rend. 49, 54) confirms this statement respecting the amalgamation of aluminium in connection with the negative pole of the battery, and adds, that if the aluminium foil is not very thick, it becomes amalgamated throughout, and very brittle. The same chemist finds that aluminium may be made to unite with mercury, merely by the use of caustic potash or soda, without the intervention of the battery. If the surface of the metal be well cleansed and moistened with the alkaline solution, it is immediately wetted by the mercury and forms a shining amalgam on the surface.

The amalgam of aluminium instantly loses its lustre when exposed to the air—becoming heated and rapidly converted into alumina and metallic mercury. It decomposes water with evolution of hydrogen, formation of alumina, and deposition of mercury. Nitric acid attacks it with violence. (Tissier).

To *gild* aluminium, 8 grammes of gold are dissolved in aqua regia, and the solution is diluted with water, and left to digest till the following day, with a slight excess of lime. The precipitate, consisting of aurate of lime with excess of lime, after being well washed, is treated at a gentle heat with a solution of 20 grammes of hyposulphite of soda. The filtered liquid serves for the gilding of aluminium, without the aid of heat or electricity, the aluminium being simply immersed in it after having been well cleaned by the successive use of potash, nitric acid, and pure water. (Tissier.)

It is somewhat difficult to solder aluminium, partly because no flux has yet been found that will clean the surface without attacking either the aluminium or the solder—partly because the surface of the aluminium is not easily *wetted* by metals more fusible than itself. An imperfect soldering may indeed be effected by means of zinc or tin; but a better method, devised by M. Hulot, is to coat the aluminium with copper by the electrolytic method, and then solder in the ordinary way. (Deville.)

Aluminium combines readily with *silicon*, and in all proportions. When very strongly heated in contact with any siliceous substance, such as glass, clay, or earthenware, it invariably reduces the silicon and unites with it. Nevertheless, aluminium may be fused in glass vessels or earthen crucibles without undergoing the slightest alteration, provided no flux is used, because it does not then come into intimate contact with the substance of the vessel; but the instant a flux is added, decomposition takes place. The properties of the compound vary according to the proportion of silicon present. An alloy containing 10·3 per cent. of silicon, called *cast aluminium* (*fonte d'aluminium*), is of a grey colour and very brittle. A compound containing as much as 70 per cent of silicon, still exhibits metallic properties. A small proportion of silicon does not deteriorate aluminium so much as an equal proportion of copper or iron. All the compounds of aluminium and silicon are much more easily altered by exposure to the air and by the action of acids and alkalies than either pure aluminium or pure silicon.

Boron unites with aluminium under the same circumstances as silicon and alters its properties in a similar manner. When aluminium is fused with boracic acid at a high temperature, the boron

is separated in transparent red or yellow octohedral crystals, which in lustre, refractive power, and hardness, are scarcely inferior to the diamond.

Aluminium does not appear to be capable of combining with *carbon*.

STANNATES OF SODA AND POTASH.

THE protoxide and binoxide of tin are both capable of forming crystallizable salts with bases. The salts thus formed by the protoxide or stannous acid (SnO) are called *Stannites*, and those formed by the binoxide or stannic acid are called *Stannates*. It is with these latter that we are here chiefly concerned.

The stannates of ammonia, potash, and soda, are soluble in water; all the rest are insoluble. The stannates of the fixed alkalies and alkaline earths are obtained by heating binoxide of tin with the hydrates of potash, soda, baryta, &c., or with the corresponding nitrates, chlorides, or sulphides; also by boiling hydrated stannic acid (obtained by precipitation from bichloride or bisulphate of tin) with a caustic alkaline lye. The insoluble stannates may be prepared by precipitating a solution of stannate of soda or potash with a salt of the required metal: *e.g.*, stannate of lead by precipitating stannate of soda with acetate of lead.

The stannates are decomposed by all acids, even by carbonic acid, the stannic acid being separated in the form of a hydrate. The stannates of soda and potash are decomposed by ignition into anhydrous stannic acid, and alkali retaining a small quantity of that acid.*

The stannates of soda and potash, especially the former, are extensively used as mordants in dyeing and calico-printing; and

* There is another class of stannates, called *metastannates*, which are produced by the action of caustic alkalies on the modification of binoxide of tin (metastannic acid) obtained by the action of nitric acid on metallic tin. The formula of the metastannates is (MO . 4 HO) Sn^4O^{10} (M denoting a metal), and they cannot be deprived of their basic water without decomposition; whereas the stannates (MO . SnO^2) can exist either in the hydrated or the anhydrous state. The metastannates of potash and soda, when heated with excess of base, are transformed into ordinary stannates. All the modes of preparation described in the following pages relate to the stannates. The metastannates are not of any commercial importance.

several patents have been taken out for their economical preparation on the large scale. The most important are those of Mr. James Young* (formerly of Manchester, now of Glasgow), which include the following processes:—

1. To make stannate of soda:—A quantity of tin ore, or what is commonly known in Cornwall by the name of "black tin," reduced to powder, is put into an iron pot along with a solution of caustic soda, and the pot is set on a fire to boil. The proportions in which these ingredients are used vary with their respective qualities. An ore containing, say, 70 per cent. of tin, will require about 2½ times its weight of caustic soda-liquor containing about 22 per cent. of soda—the proportion of the liquor employed increasing or diminishing according as it is desired to produce a stannate with a greater or less excess of alkali. The materials are well stirred, and the heat is gradually raised to between 500° and 600° Fahrenheit, at which temperature the ore is acted on by the soda, and the tin or oxide of tin, or the greater part of it, combines with the soda. The progress of the operation may be known from time to time by taking out of the pot a small portion of the mass, and ascertaining how much of it dissolves in water. The hot mass is then transferred from the pot to another vessel, and set to cool, and when cooled it is mixed with water, when any insoluble matters which may have remained in it unaffected by the caustic soda, are easily separated by filtration or by subsidence. The clear liquor which remains is the stannate required, which may be either employed in that state or evaporated to dryness, or crystallized—the solid salt being dissolved as required for use.

2. Stannate of soda is prepared by mixing a quantity of tin ore reduced to powder with 1½ times its weight of nitrate of soda, subjecting the mixture to a red heat in an iron vessel, passing a current of steam over it, and keeping it constantly stirred during the operation, in order to expose fresh portions of it to the action of the steam. Nitric and nitrous acids are given off in fumes, which may be condensed with water, and collected as collateral products (reducing thereby the cost of the stannate). A stannate remains, which may be freed from its insoluble impurities by mixing with water, and filtration or subsidence, as in the process first described; and it may also either be left in a state of solution, or crystallized, or evaporated.

* Dec. 9th, 1848, No. 12,359; and August 16th, 1849, No. 12,744.

3. The nitrate of soda, employed in the last process, may be replaced by chloride of sodium (common salt), using, however, equal weights of the salt and tin ore, and pursuing the same operations in all other respects. Stannate of soda is thereby obtained with muriatic acid as the collateral product.

4. The following process yields both stannate and stannite of soda:—A quantity of metallic tin is heated to redness with an equal weight of solid hydrate of caustic soda, which may be obtained by boiling down caustic soda-liquor (say, 3½ cwt. of the liquor containing 22 per cent. of soda to about 1 cwt. of the hydrate), stirring the materials well during the operation—whereupon the water of the hydrate of soda becomes decomposed and parts with its oxygen to the tin, and the oxide of tin so formed, uniting with the soda, forms a stannite of soda suitable for some dyeing and printing purposes. To convert this stannite of soda into stannate, it is boiled in water, whereupon a portion of metallic tin is precipitated in the form of a black powder, and the solution remaining is stannate of soda;—or, 20 parts of metallic tin, 16 parts of solid hydrate of caustic soda, and 3 parts of oxide of manganese (all by weight), are subjected to a red heat in an open pot, keeping the mixture constantly agitated, and allowing a free access of air. So small a proportion of oxide of manganese as is contained in this mixture, would be quite insufficient of itself to peroxidize all the tin; but this oxide of manganese is converted by the heat and by absorption of oxygen from the atmosphere into a manganate of soda, and this manganate becomes decomposed by the tin; part of the oxygen goes to form peroxide of tin, and a residuum of oxide of manganese is left, which becomes once more, by a new absorption of atmospheric oxygen, a manganate; and this manganate is decomposed by the tin as before, yielding a fresh accession of peroxide of tin; and so the process goes on until all or nearly all the tin has become peroxidized and combined with the soda. The mass in the pot is then dissolved in water, and the solution clarified by filtration or subsidence. The supernatant liquor is a solution of stannate of soda, which may either be left as it is, or crystallized, or evaporated to dryness, as above. The precipitated oxide of manganese may be collected and used over again.

The stannite formed in the first of the processes just described, may be converted into stannate of soda, by merely keeping it freely exposed, at a red heat, to the atmosphere for a sufficient length

of time; but the oxidizing process by means of manganese is more expeditious and, on the whole, cheaper.

5. Stannate of soda may also be prepared from oxide of tin, obtained by heating metallic tin to redness in an iron vessel, keeping it well stirred, and passing a current of steam or air over it, this oxide of tin being treated with caustic soda in precisely the same way as the ore.

6. Stannate and stannite of potash may be prepared by precisely similar methods, substituting only in each case, where caustic soda, or nitrate of soda, or chloride of sodium is directed to be employed, an equivalent of caustic potash, or of the chloride of potassium.

7. Stannate of soda or potash may be prepared by heating tin ore with sulphide of sodium or potassium, and afterwards separating the sulphur. To obtain sulphide of sodium, about 22 parts by weight of dry sulphate of soda and 7 parts by weight of small coal are mixed together and heated to redness in a reverberatory furnace. The material is to be stirred from time to time during the heating, which is to be continued until the fused mass ceases to emit any inflammable gases. The residuum left in the furnace is then to be taken out, and when cooled is to be washed in water, so as to dissolve out the sulphide of sodium. The solution may be filtered and evaporated to dryness, or nearly so, and the product thus obtained will be sulphide of sodium. Sulphide of potassium may be made in precisely the same manner, substituting about 27 parts by weight of sulphate of potash for the sulphate of soda.

In order to obtain stannate of soda from tin ore by this process, about 20 parts by weight of the ore (containing from 80 to 90 per cent. of peroxide of tin) are mixed with about 12 parts by weight of dry sulphide of sodium, or, if moist, a proportionably larger quantity; and to obtain a stannate of potash, about the same quantity of ore with about 17 parts by weight of dry sulphide of potassium, or, if moist, a proportionably larger quantity. These materials should be well mixed together, and, if dry sulphide has been used, about 6 parts of water are added to the mixture. The materials are then to be dried in any convenient manner, after which they are to be heated to redness in a reverberatory furnace, and kept at that temperature until the whole or nearly the whole of the peroxide of tin has been converted into a compound soluble in water. Two hours will gene-

rally be sufficient to produce this effect, and, if desired, the progress of the operation may be ascertained by withdrawing, from time to time, a small portion of the materials from the furnace, and washing it in water. The appearance of the unchanged ore (if any) remaining in the material when thus washed, will be sufficiently apparent. When the ore has been sufficiently acted upon, the remaining mass of material is to be removed from the furnace, and when sufficiently cool it must be washed with hot water to separate the soluble product from any insoluble matters with which it is mixed. The solution is to be purified from any insoluble matters or impurities by subsidence or filtration. To procure the stannate of soda or stannate of potash from the clear solution thus obtained, it is necessary that the sulphur contained in the solution should be separated from the other materials contained in it, and replaced by an equivalent of oxygen; and any chemical agent may be employed which will effect this purpose without combining with the stannate of soda or potash, or either of its elements. For this purpose, it is best to use some one of the metallic oxides, such as the hydrated oxide of manganese, the hydrated oxide of iron, or oxide of copper, and to boil the clear solution obtained, as before mentioned, with the oxide, until the whole of the sulphur contained in it has been separated. The best and cheapest material for the purpose is the hydrated oxide of manganese which has been precipitated or separated from a combination with an acid, such as oxide of manganese separated from the chloride of manganese by lime. The quantity of this hydrated oxide of manganese required is such as will be equivalent to 11 parts by weight of the dry oxide to the quantity of soluble material produced from 20 parts by weight of tin ore, as before mentioned. The quantity of hydrated oxide of iron, or of oxide of copper, if used, should be equivalent to the before-mentioned quantity of oxide of manganese. The solution before mentioned is to be heated with the metallic oxide, the whole being continually stirred until all the sulphur is separated from it; and in order to ascertain when the process is complete, a portion of the solution is tested from time to time by a salt of lead or any ordinary test for sulphur, the process being continued, and, if necessary, more of the metallic oxide added, till the solution ceases to show, when tested, any trace of sulphur. The solution thus separated from sulphur will contain stannate of soda or potash, as the case may be, with a portion of free alkali; and the solution

may be separated from the insoluble matters mixed with it by means of a filter, or by allowing the insoluble matters to subside, and then drawing off the clear solution. The clear solution thus obtained may, if required, be evaporated in any convenient manner so as to obtain the stannate of soda or potash in a dry or a crystallized state.

8. Another method of producing stannate of soda or stannate of potash, is to subject a mixture of tin ore with lime, baryta, or strontia, to a high degree of heat in a reverberatory furnace, and, after removing the alkaline earth from the product thus obtained, to combine the remaining peroxide of tin or stannic acid with soda or potash. In performing this process with lime, 4 parts by weight of quicklime are slacked and reduced to a pulp with water, and then intimately mixed with 6 parts by weight of tin or black tin of the description already mentioned, and reduced to powder. The mixture is then dried and heated to a full red heat in a reverberatory furnace for about four hours, till all or nearly all the peroxide of tin contained in the ore is capable of being dissolved in hydrochloric acid. The mixture, after being removed from the furnace and allowed to cool, is to be mixed with such a quantity of hydrochloric acid as will be equivalent to 15 parts by weight of hydrochloric acid of specific gravity 1·175 mixed with an equal quantity of water. The mixture being well stirred up in this dilute acid, the lime which it contains will dissolve in the acid and form chloride of calcium, which is to be separated from the undissolved residue, consisting of peroxide of tin mixed with some other matters. This separation may be effected by filtration, or by allowing the undissolved matters to subside, and then drawing off the watery solution; after which the undissolved matters must be washed with water until the whole of the chloride of calcium has been removed. If baryta is used instead of lime, the proportion (if anhydrous) must be about $2\frac{3}{4}$ times the weight of the lime; and if hydrated, greater in proportion; and if strontia is employed, the quantity of it must be chemically equivalent to the quantities of lime and baryta already mentioned. It is to be observed that the hydrochloric acid directed to be employed in performing this process, is used for the purpose of removing the alkaline earth from the peroxide of tin; and although the quantity of acid must be sufficient for that purpose, yet care should be taken not to use any excess, because it would,

in that case, combine with and dissolve some of the peroxide of tin.

To make stannate of soda or potash, the peroxide of tin obtained by the process thus described is to be boiled in 10 parts by weight of caustic lye, containing 22 per cent. of soda or 32 per cent. of potash. The boiling is, in either case, to be continued until the alkali has taken up all or nearly all the peroxide or stannic acid capable of entering into the combination, the quantity of which will depend upon the perfection of the process to which the ore has been subjected. A soluble stannate of soda or potash with an excess of alkali will be formed in this manner, which is then to be diluted with water and separated from the insoluble matters by filtration or any other convenient means: and the solution may be evaporated to dryness, or not, as may be required.

In preparing stannate of lime, baryta, or strontia, as above described, the nitrate or chloride of calcium, barium, or strontium, may be used instead of the earths themselves, just as in the preparation of the stannates of potash and soda (pp. 35, 36).

9. Another mode of producing stannate of soda or stannate of potash, is to boil in a solution of sulphate of soda or potash the product obtained by subjecting a mixture of tin ore and baryta to a high degree of heat in a reverberatory furnace. To make stannate of soda by this process, about 11 parts of dry sulphate of soda are dissolved in a convenient quantity of water, and mixed (to facilitate the operation) with about 3 parts by weight of caustic soda-liquor (containing 22 per cent. of caustic soda); to this solution is added the product obtained by heating 6 parts of tin ore with 11 parts of baryta in a reverberatory furnace, as already mentioned, the product being first reduced to a state of powder. The solution containing this powder is now to be boiled in an iron or other convenient vessel for about four hours, or until all or nearly all the stannic acid capable of entering into combination with the alkaline base of the sulphate of soda has been separated from the baryta. When this boiling has been completed, a stannate of soda with excess of caustic soda will remain dissolved in the liquor, and the sulphate of baryta (insoluble or nearly so) formed during the process will fall down to the bottom of the vessel. The solution of stannate of soda is then to be separated from the insoluble matters with which it is mixed, and crystallized

or evaporated to dryness or not, as may be required. A precisely similar process serves for the preparation of stannate of potash.

10. *Preparation of Stannate of Lime, Baryta, or Strontia, by Precipitation.*—To produce stannate of lime, stannate of soda is dissolved in any convenient quantity of water, and lime is added in the proportion of 38 parts by weight of quicklime to 143 parts by weight of the dry stannate of soda contained in the solution. The lime is first slacked with water and reduced to a pulpy consistence, and then mixed with the solution of stannate of soda. The mixture is then to be boiled in any convenient iron vessel until the whole of the stannate of soda is decomposed, and the stannic acid or peroxide of tin combined with the lime, which will usually be effected in about an hour. The stannate of lime thus formed is precipitated to the bottom of the vessel, and caustic soda remains in solution, which may be used in again forming stannate of soda from tin ore, or for any other purpose to which it may be applicable. To ascertain whether the whole of the stannate of soda has been decomposed, a small portion of the liquid is from time to time taken out of the vessel, filtered, and treated with a few drops of clear lime-water. If the lime-water produces a cloud, the boiling is continued, and, if necessary (which, however, seldom happens), more lime is added to the boiling mixture, until a portion of it, when tested, fails to show any cloudiness. The stannate of lime thus formed may be separated from the solution of soda by filtration or subsidence and then washed with water, after which it may, if desired, be obtained in a state of powder by drying it in any convenient manner. If the stannate of lime be made from a stannate of potash, in the manner just described, the quantity of stannate of potash used must be chemically equivalent to the quantity of stannate of soda above mentioned. The process just described may also be performed with carbonate of lime instead of quicklime, the carbonate of lime being reduced to powder. The soda resulting from this process, when carbonate of lime is used, is not caustic soda, but carbonate of soda, and the process is, on the whole, less advantageously performed with carbonate of lime than with quicklime. In like manner stannate of baryta or strontia may be prepared.

From stannate of lime, baryta, or strontia made in this manner, a peroxide of tin or stannic acid may be obtained in a state of great purity by the action of hydrochloric acid, as described at p. 39. This peroxide may be smelted in the manner usually adopted for

smelting tin ore, and in this way metallic tin of great purity may be obtained.

The processes above described for obtaining stannate of soda and stannate of potash will produce those materials mixed with some free alkali or an excess of alkali. No method of separating those materials from the free alkali is given, because, for the purposes to which they are generally applied, they can be more beneficially used when mixed with such a portion of free alkali.

11. Binoxide or peroxide of tin may be prepared by passing carbonic acid gas into a solution of stannate of soda or potash, or over either of these salts, either in the dry or in the damp state, the alkaline carbonate thereby produced being afterwards removed by washing with water. The binoxide may also be precipitated from the solution by sulphuric acid, or by bicarbonate or bisulphate of soda or potash.

The oxide obtained in this manner, or from the stannates of the alkaline earths, may be used for preparing the persalts of tin or stannic salts; thus the bichloride $SnCl^2$ (or in solution $SnO^2.2HCl$) may be obtained by dissolving the binoxide in hydrochloric acid.

For the tin ore and metallic tin used in some of the preceding processes, the refuse of the tin smelting works, called tin slag, may occasionally be substituted with advantage. It is to be reduced, like the ore, to powder, and used either with soda or potash, or with the nitrates or chlorides, or with the alkaline earths or their salts, or with soda or potash and oxide of manganese, as the case may be. (Young.)

Dr. Richardson, of Newcastle, uses for the preparation of stannate of soda, the mixed oxide of lead and tin obtained in refining the hard leads of commerce. These alloys of lead and tin, which are sometimes sold as waste products, are exposed to a current of hot air in a reverberatory furnace, either in the melted state, or in sheets, or in lumps, granulated or not, till they are converted into oxides. These mixed oxides are then treated with acetic or nitric acid, whereby a solution of acetate or nitrate of lead is obtained, and binoxide of tin remains, which may then be converted into stannate of soda by any of the processes already described. Alloys of tin and copper may be oxidized in like manner, and the oxide of copper dissolved out by acetic or sulphuric acid.

Mr. Edward Haeffely, of Radcliffe, Lancashire, prepares stannate of soda by decomposing plumbate of soda with metallic tin. Litharge or red lead is heated in a metal pan with a solution of caustic soda containing about 22 per cent. of alkali, and the liquid is diluted with water or with the washings afterwards mentioned, sufficiently to hold in solution the stannate of soda subsequently formed. In the solution of plumbate of soda thus produced, feather metallic tin is suspended, whereupon the lead is precipitated as a spongy metallic mass, while the tin takes its place in the solution, converting the plumbate of soda into stannate. The proportions used are 16 lbs. of tin, 45 lbs. of caustic soda, of 70° (Twaddell), and 70 to 80 lbs. of litharge or 54 lbs. of red lead. When the tin has entirely disappeared, which will be after 4 or 5 hours' boiling, the fire is withdrawn and the precipitate left to settle. The clear solution of stannate of soda is then decanted, and the precipitate washed with one or two waters, the washings being used for diluting the alkali in subsequent operations. The precipitate is thrown on a plate of hot iron or other metal, and the temperature is raised nearly to redness. The lead is then speedily reoxidized by the air and converted into litharge or red lead, which is then ready for another operation.

Instead of oxide of lead, hydrated sesquioxide of iron, hydrated binoxide of manganese, manganate of soda, indigo, and other oxidizing substances may be used. The precipitates thereby formed will be protoxides, which may afterwards be reconverted into the higher oxides and used over again. Blue indigo will be reduced to white indigo.

The patentee claims, as his invention, "the production of the *stannates of soda, potash, and ammonia*, by forming stannic acid by the oxidation of tin in an alkaline solution by the agency of oxide of lead or any other oxide having a less affinity for oxygen than tin." *

Mr. John Dale, of Manchester, converts *protosalts of tin* (stannous salts) into *persalts* of tin (stannic salts) by the oxidizing action of the gases evolved by the decomposition of nitric acid, using for the purpose the waste gases given off in the conversion of arsenious acid into arsenic acid by the action of nitric acid. The products thus obtained may either be used as persalts of tin

* Patent, Sept. 21st, 1855, No. 2,122.

(stannic, chloride, sulphate, &c.) or they may be precipitated by alkalies or alkaline carbonates, and the binoxide of tin thus produced may be converted into stannate of potash or soda, by the action of caustic alkalies as already described.

VALUATION OF TIN ORES.*

A. *In the dry way:*

1. Pure tin-stone, with only a small quantity of earthy matters, is mixed with 5 to 10 per cent. of pearlash or black flux, and 5 to 25 per cent. of borax, in a crucible lined with charcoal and heated to whiteness in an air-furnace for 45 to 75 minutes; the tin should then be fused into a button.

2. Tin-stone, in combination with earthy substances, must be prepared for reduction by trituration and levigation in a cylindrical glass vessel.

3. Tin-stone largely contaminated with sulphides, arsenides, and antimonides, is first thoroughly roasted on a test (*Röstscherben*); the product is freed from the oxides of other metals by digestion in hydrochloric acid, which does not attack the tin-stone; and the residue is collected on a filter, washed with hot water, and dried. One part of the ore thus purified is mixed with 1 to 2 parts of black flux or a mixture of charcoal dust and carbonate of potash, or with flour and 25 to 40 per cent. of borax. The mixture is introduced into a crucible of refractory clay, then covered with a layer of common salt, and the crucible is fitted with a lid of black lead ware, which does not close it completely—a condition which is essential to ensure the reduction of the tin by formation of carbonic oxide. A lump of charcoal may also be laid on the salt. The crucible is heated to whiteness for 45 to 75 minutes in an air-furnace, then left to cool, and the button of tin cleaned from slag and weighed. Its purity may be known by its peculiar colour, its malleability, and by the entire absence of magnetic properties. According to Berthier, the roasting of the ore may be dispensed with by boiling it for a few minutes with aqua regia. But for ores containing much sulphur, the process above given is to be preferred.

* Handbuch der metallurgischen Hüttenkunde, von Bruno Kerl, ii. 362.

B. *In the wet way* (Volumetric methods):

1. Gaultier de Claubry* converts 0·590 gramme of the ore to be tested, into protochloride of tin, by treating it with hydrochloric acid or aqua regia, and boiling the solution with metallic iron; and treats the strongly acid solution with a standard solution of iodine in alcohol (1·260 grm. iodine to 100 cub. cents.† alcohol of 95 per cent), till the presence of free iodine is indicated by its brown colour, or by the blueing of starch added to the liquid:

$$SnO + I + HO = SnO^2 + HI.$$

The number of cubic centimetres of the solution used correspond to the per centage of tin.

2. Mène‡ treats the tin ore (0·590 grm.) with aqua regia; reduces the resulting bichloride of tin to protochloride by boiling with zinc; and adds a standard solution of sesquichloride of iron containing 0·56 grm. (=2 equivalents of iron) in 100 cub. cents., as long as the yellow colour of that solution is destroyed, or till a permanent blood-red colour is produced in the liquid previously treated with a drop of sulphocyanide of potassium. The number of cubic centimetres of the iron solution used, gives directly the number of parts by weight of tin in a hundred:

$$SnCl + Fe^2Cl^3 = 2FeCl + SnCl^2.$$

The presence of arsenic interferes with the action of this test.

3. Penny§ decomposes the solution of protochloride of tin with a standard solution of bichromate of potash:

$$3\,SnCl + 2CrO^3 = 3\,SnO^2 + Cr^2Cl^3,$$

and detects the completion of the reaction by means of acetate of lead, or by the reddening of a mixture of protosulphate of iron and sulphocyanide of potassium. Schwarz¶ recommends the substitution of manganate of potash (mineral chamæleon) for the bichromate; and Streng‖ and Peter Hart** use iodide of potassium and starch-paste to indicate the completion of the

* Dingler's Polytechn. Journal, cii. Heft 2. Schwarz, Maassanalysen, 1853, p. 73.

† If English measures be preferred, it is merely necessary to substitute *grains* for grammes, and *grain-measures* for cubic centimetres; *e.g.*, instead of 1·260 grm. and 100 cub. cents., 12·6 grains and 1000 grain-measures might be used.

‡ Dingler, cxvii. 230; Schwarz, 1853, p. 132.

§ Chem. Soc. Qu. J. iv. 239.

‖ Pogg. Ann. cxii. 62.

¶ Maassanalysen, c. 50, p. 133.

** J. pr. Chem. lxii. 378.

action. The amount of tin is calculated, according to Streng, by the following formula:

$$x = \frac{3Sn.100.c.C}{(KO.2CrO^3) \times A}$$

where C denotes the number of cubic centimetres of the solution of chromate used; c, the quantity of solid bichromate in 1 cub. cent. of the solution; A, the quantity of the tin compound taken; and x, the required per centage of tin.

[For Plattner's quantitative methods by the blowpipe, see *Plattner on the Blowpipe*, translated by Muspratt.]

ANALYSES OF TIN ORES.

Tin-stone, in the form of wood-tin and in rounded crystals, from the auriferous sand of the County of Wicklow, in Ireland, contains, according to an analysis by W. Mallet (Phil. Mag. [3] xxxvii. 394)—

Binoxide of tin . .	95·26
Sesquioxide of iron .	2·41
Silica	0·84
	98·51

Bergemann (Jahrb. Miner. 1857, 895) found in dark brown *wood-tin*, from Xeres, in Mexico—

Binoxide of tin . .	89·427
Sesquioxide of iron .	6·628
Alumina	1·200
Silica	2·215
	99·470

Tin pyrites:—

	a	*b*
Tin . . .	25·65 . .	26·85
Copper . .	29·38 . .	29·18
Iron . . .	6·24 . .	6·73
Zinc . . .	9·68 . .	7·26
Sulphur . .	29·05 . .	29·46
Matrix . .		0·16
	100·00	99·64

a from Zinnwald, analysed by Rammelsberg (Pogg. Ann. lxxxviii. 603); *b* from Saint Michael's Mount, analysed by J. W. Mallet (Silliman's Journal [2], xvii. 33).

TUNGSTATES OF SODA AND POTASH.

TUNGSTIC acid unites with the alkalies and other metallic oxides in several proportions, forming both neutral and acid salts. The alkaline and earthy tungstates are colourless. The tungstates of potash, soda, ammonia, lithia, and magnesia, are soluble in water; the rest are insoluble. All the salts of tungstic acid are insoluble in alcohol, have a very high specific gravity, and are decomposed by the stronger acids.

The soluble neutral tungstates, *e. g.*, tungstate of soda ($NaO.WO^3$) and tungstate of potash ($KO.WO^3$), treated with sulphuric, hydrochloric, nitric, phosphoric, or acetic acid, yield a white precipitate, consisting of tungstic acid containing a small quantity of the alkali and of the precipitating acid. This precipitation is not produced by oxalic, tartaric, or citric acid. The precipitate formed by hydrochloric or nitric acid becomes yellow after some time, and more quickly if heated. The insoluble tungstates are also decomposed by sulphuric, nitric, or hydrochloric acid, yielding either pure tungstic acid in the form of a yellow powder, or a white compound of tungstic acid, the nature of which has not been clearly ascertained. A solution of an alkaline tungstate supersaturated with sulphuric, hydrochloric, phosphoric, oxalic, or acetic acid, yields, on the introduction of a piece of zinc or tin, a beautiful blue precipitate, consisting of an oxide of tungsten containing less oxygen than tungstic acid. A solution of an alkaline tungstate, mixed with a soluble salt of barium, calcium, zinc, lead, mercury, or silver, forms a white precipitate consisting of tungstate of barium, calcium, zinc, &c.

There are several classes of *acid* tungstates, and, according to Laurent (Ann. Ch. Phys. [3], xxi. 54) they contain different modifications of tungstic acid, distinguished from one another by their solubility in water and other physical characters. Laurent distinguishes the following classes of tungstates:

1. *Ordinary tungstates*, $WO^3.MO$ with or without water (M denoting a metal). To this class belong the neutral potash, soda, and baryta salts, and most of the insoluble tungstates. No acid salts of this class appear to exist. The solution of an ordinary tungstate dropped into excess of dilute nitric acid, produces a gelatinous precipitate. 2. *Paratungstates*, $4WO^3.2MO$, with or without water. To this class belong the salts commonly called

bitungstates of potash, soda, ammonia, baryta, &c. They all, excepting the soda-salt, dissolve but sparingly in water. The solutions give no precipitate on the addition of very small quantities of nitric acid, or of very weak hydrochloric acid. They give precipitates with the ammoniacal solutions of nitrate of magnesia, zinc, and silver, which the ordinary tungstates do not. 3. *Metatungstates*, $3WO^3.MO$, with or without water. The soluble salts of this variety are formed by boiling a solution of a paratungstate for several hours; the solution is not precipitated by concentrated hydrochloric acid. 4. *Isotungstates*, $2WO^3.MO$, with or without water: formed by boiling an alkaline metatungstate with excess of alkali; they are but slightly soluble in water. The acid, which may be separated from them by sulphuric or hydrochloric acid, is chiefly characterized by reproducing an isotungstate when treated with caustic alkali. 5. *Polytungstates*, $6WO^3.3MO$. When yellow tungstic acid, obtained from wolfram by the action of a stronger acid, is treated with caustic alkali, and the solution slowly evaporated, a paratungstate is first deposited, and afterwards an isotungstate. The mother-liquor separates into two layers, one of which is brown and syrupy, and, when boiled with strong nitric or hydrochloric acid, yields a precipitate, which is not gelatinous and does not turn yellow when boiled. Polytungstic acid is further characterized by forming with ammonia a very soluble salt, which becomes gummy by evaporation.

The soluble tungstates are used as mordants in dyeing, in the same manner as the stannates. The salt generally employed for this purpose is the neutral tungstate of soda ($NaO.WO^3$), the preparation of which for use in dyeing and calico-printing has been patented by Mr. Robert Oxland, of Plymouth.*

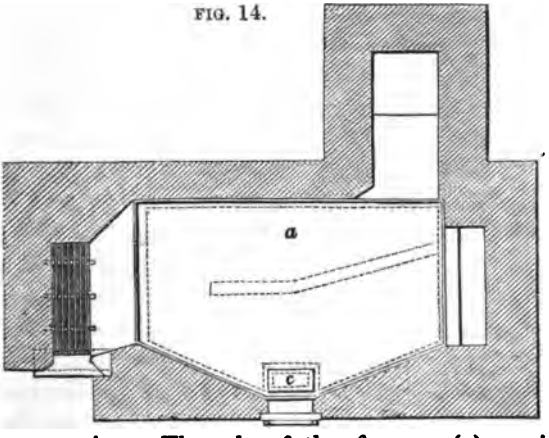
The ore of tungsten used in the preparation is *wolfram*, the native tungstate of iron and manganese; native tungstic acid may also be used if it can be obtained in sufficient quantity. Wolfram is found either alone or, more frequently, associated with tin ores. When the tin ores are used, they are to be dressed in the usual manner till ready for smelting. The proportion of wolfram present in the ore having been ascertained by analysis, and the ore well dried, it is mixed with common alkali or soda-ash (the alkalimetric value of which has been previously ascertained) in

* September 2nd, 1847, No. 11,848.

the proportion of the chemical equivalents (31 parts of anhydrous soda, NaO, to 120 parts of tungstic acid, WO^3). For example, if the ore contains 20 per cent. of wolfram, every 100 parts of such ore will contain 15 parts of tungstic acid, and will require $3\frac{1}{2}$ parts of soda, so that if the soda-ash contains 50 per cent. of soda, the quantity of it required will be 7 parts.* The ore and alkali having been thoroughly mixed, the charge may be put into the furnace. Sulphate of soda or salt-cake may also be used instead of alkali; it is cheaper, but the alkali has the advantage of rendering the process more manageable by inexpert workmen. The salt-cake, in fine powder, is to be used in the proportion of 8 parts for 7 of alkali of 50 per cent., mixed with $\frac{1}{4}$ of its weight of coal in fine powder, and is to be combined with the ore in the same manner as when alkali is used; but when the charge is in the furnace, it requires to be exposed to the action of heat longer than when alkali is used, or until all appearance of combustion has ceased.

The best form of furnace is shown in the annexed figures, Fig. 12 being a plan, Fig. 13 a longitudinal section, and Fig. 14

FIG. 14.

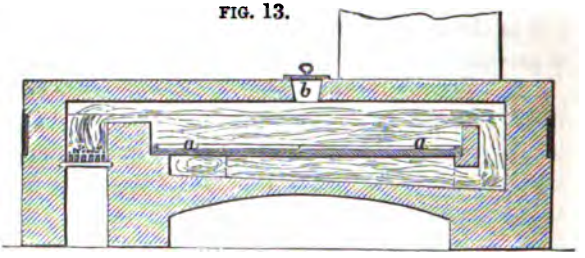


a transverse section. The sole of the furnace (*a*) consists of a cast iron plate cast in two pieces, the joint being formed across

* The above is the calculation given in Oxland's specification. It is not quite exact; for wolfram ($MnO.3FeO.4WO^3$) contains 77·3 per cent. of tungstic acid (WO^3). Hence the quantity of tungstic acid in 20 parts of wolfram is $20 \times \frac{77{\cdot}3}{100} = 15{\cdot}46$ parts; and the quantity of soda (NaO) required to decompose it, is $15{\cdot}46 \times \frac{31}{120} = 4$ parts; so that if soda-ash of 50 per cent. be used, the quantity required will be, not 7, but 8 parts. [EDS.]

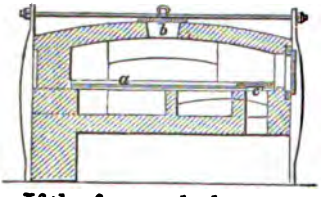
the breadth of the furnace. The length is 9 feet, the breadth in the widest part 6 feet, and it is 1 inch thick throughout. The fire passes over the plate, returns below and circulates beneath it, as shown in the plan, before it passes away to the main flue or chimney. The furnace is charged through the hole *b* in the top, and the charge is drawn through the hole *c* in the sole *a*, from which, through the flue beneath into the arch below, a communication is

FIG. 13.



opened, which may be covered, when the charge is not being drawn, by a small plate of iron, which is always kept in the furnace.

FIG. 14.



According as the ore may be coarse or fine-grained, the charges will vary from 6 cwt. to 10 cwt. of ore, with its complement of alkali. The coarse-grained ore may be put into the furnace in the largest quantity.

If the furnace be kept at a good red heat, and the charge be well managed, 8 charges per diem of 24 hours may be drawn. The charge is to be turned over from time to time as it lies in the furnace, in order to get it equally hot throughout; but as the front part of the charge, or that nearest to the fire, will be ready first, a portion of the charge may be first drawn, another portion of it turned forward to the fire, and so successive portions drawn until the whole of the charge is removed. If the charge has been thoroughly worked in the furnace, it will be found that, as soon as the red heat has disappeared, it will have caked into a hard mass, which should be broken into lumps before it gets too cold.

The charge drawn from the furnace will consist of the native oxide of tin, the soluble tungstate of soda, with the oxides of iron and manganese, and a small proportion of silica.

In order to separate these substances from each other, the following process of lixiviation is to be adopted:—3 vats of wood or

iron of suitable dimensions, say, 5 feet long, 3 feet wide, and 3 feet deep, or of any other form and of similar capacity, may be arranged side by side, and below each a vessel of about one-third the capacity of the vat, to receive the liquid running down from the vat. In the bottom of the side of the vat, immediately over the receiver, should be a plug-hole.

On the interior of the vat, in front of this hole, should be placed a filter, consisting of a little straw or tow, over which a piece of metal, pierced with holes, is placed, and kept down by a few clean stones. The first vat being partially filled with water, the charge, when cooled down to a black heat, is thrown into it until it is very nearly full. The vat is then filled up with water, and after standing about half an hour, the plug is partially drawn, and the clear solution of tungstate of soda is allowed to run down into the receiver, whence it is removed into the evaporating pans. For testing the strength of the solutions, and to determine thereby when the whole of the soluble matters have been removed from the ore, Twaddell's hydrometer is used. As the liquor runs down, the vat should be kept filled up with water; but when the liquor in the receiver is reduced to the strength of 25 of the hydrometer, it should be no longer removed to the evaporating pan, but pumped up into the second vat for commencing the lixiviation of the next lot of calcined products from the furnace, instead of employing water alone. The weaker solutions from No. 2 are passed on to the fresh charge in No. 3 vat—No 2 being continually filled up with liquor running down from No. 1, until the hydrometer no longer indicates the presence of any saline matter in it, or, at most, not more than two or three degrees. The strong solution obtained as just described, should be concentrated in iron evaporating pans, until brought up to the crystallizing point, indicated by the formation of a permanent saline crust on the surface of the liquor, which is then to be removed to suitable coolers and allowed to remain till the crystallization is completed. The crystals should be removed and the mother-liquor mixed with other liquor in the evaporating pans, for crystallization.

The neutral tungstate thus obtained may be used either alone or in combination with acids. In the latter cases, it must be first dissolved in a quantity of water much larger than is necessary for its mere solution—say, 1 ounce of the salt in a quart of water. The acid may then be added till all the alkali is saturated and the acid is found in slight excess.

Wool, either in skein or piece, may be dyed by first boiling in such a solution as that just described, in which nitro-muriatic acid has been employed, and subsequently in the dye-bath; or the acidulated solution of the tungstate may be at once mixed with the dye, and the cloth boiled with the mixture without any other previous preparation than the usual cleaning with logwood as the dye. By such treatment as the foregoing, a violet colour is produced, passing into a claret, and finally, if the boiling be continued, into a black. (Oxland.)

Mr. F. G. Spilsbury* prepares ordinary tungstate of soda or potash by boiling wolfram, tungstate of lime, or native tungstic acid, with caustic potash or soda under pressure; also tungstic acid, by mixing wolfram or tin ores containing it with bisulphate of potash or soda, or with a mixture of neutral sulphate of potash or soda and sulphuric acid, or with a mixture of chloride of potassium or sodium and sulphuric acid, and heating the mixture to redness, till the wolfram is decomposed into tungstic acid and the sulphates of iron and manganese.

The tungstic acid thus obtained may be used for decolorizing acetic acid and acetates. A coloured solution of acetate of lime or acetate of lead is boiled with tungstic acid, whereby a precipitate of tungstate of lime or tungstate of lead is formed, which carries down the colouring matter, and colourless acetic acid remains in solution. The acetic acid may then be combined with baryta or oxide of lead, and the solution treated with tungstate of soda, yielding pure tungstate of baryta or lead, and pure acetate of soda. Impure acetate of lime may also be at once decolorized by mixing it with a solution of tungstate of soda.

A very important application of tungstate of soda has lately been made: viz., for rendering linen, cotton, and other fibrous substances, non-inflammable. Muslin, steeped in a solution containing 20 per cent. of this salt, is perfectly non-inflammable when dry. The salt acts apparently by firmly enveloping the fibre, and thereby preventing contact with the air. It is smooth and of a fatty appearance, like talcum, and therefore does not interfere with the process of ironing, but allows the hot iron to pass smoothly over the fabric. The non-fulfilment of this condition completely prevents the use of other salts, such as phosphate and sulphate of ammonia, which are otherwise efficacious in destroying inflammability, for all fabrics which have to be washed and ironed.

* Provisional Specification, June 19th, 1858, No. 1382.

The use of tungstate of soda for this purpose offers only one difficulty, viz., the formation of a bitungstate of little solubility, which crystallizes from the solution. This inconvenience may, however, be obviated by the addition of a small quantity of phosphoric acid or phosphate of soda. The best way of preparing a solution, of minimum strength for the purpose in question, is to dilute a concentrated solution of the neutral tungstate with water to 28° Twaddell, and then add 3 per cent. of phosphate of soda. This solution is found to keep and to answer well; it is now constantly used in Her Majesty's laundry. (Versmann and Oppenheim.*)

F. W. Emerson† has taken out a patent for the preparation of the acid tungstates (paratungstate, metatungstate, &c., pp. 47, 48) of potash and soda, and for their use in dyeing, and in the preparation of pigments. There is, however, nothing new in his methods of preparation. He first obtains ordinary tungstate of potash or soda by a process exactly similar to that of Oxland, then converts it into bitungstate (or paratungstate, $4WO^3.2NaO$) by adding tungstic acid to the solution of the neutral tungstate; and prepares the metatungstate, isotungstate, and polytungstate, by the methods given by Laurent (p. 48). These acid salts may be used as mordants in dyeing; or pigments may be prepared from them by precipitating with salts of lead, zinc, baryta, lime, or mixtures of the same, and grinding up the insoluble tungstates thus formed with oil, turpentine, &c.

Mr. Emerson also prepares *blue oxide of tungsten*, either by the action of zinc or tin in a solution of an alkaline tungstate mixed with excess of acid, or by subjecting tungstic acid at a low red heat to the action of hydrogen, coal-gas, or carbonic oxide (Malaguti's process; see Gmelin's Handbook, English edition, iv. 26). The product must be allowed to cool in the furnace, or else withdrawn very expeditiously into an air-tight receiver, as it is apt to degenerate in colour if exposed to the air while hot. It may be ground with oil, turpentine, or varnish, and used as a pigment. To dye the blue oxide of tungsten into textile fabrics, the stuff, either in skein or piece, is boiled in a solution of an alkaline tungstate, then dried and immersed in dilute hydrochloric, sulphuric, acetic, or other suitable acid, in which zinc, tin, or some other deoxidizing metal is placed.

* Communication read before the British Association at Aberdeen, 15th September, 1859; Pharm. J. Trans. [2], i. 385.

† Specification, May 2nd, 1859, No. 1103.

The patentee likewise states that by heating wolfram, tungstate of lime, or tungstic oxide with caustic alkalies or alkaline earths, or with their salts, he has obtained certain volatile and condensable products, which are the oxides and salts of a new metal called by him *chlorolithenium*, which metal can be separated from them by the ordinary reducing agents. The salts and oxides are also stated to be useful in dyeing and for the preparation of pigments. But the description is very unsatisfactory, and no details are given as to the extraneous matters present in the ores employed, or the composition of the alkaline or saline substances by which they were decomposed. Evidence like this is altogether insufficient to establish the existence of a new metal.

VALUATION OF ORES OF TUNGSTEN.

To determine the quantity of tungstic acid in wolfram or other ores of tungsten not containing tin, the mineral is reduced to an impalpable powder and digested with aqua-regia till it is completely decomposed: the solution is evaporated to dryness in the water-bath, and the metallic chlorides formed are dissolved out with acidulated water. The residual tungstic acid (which may also contain silicic and niobic acids) is washed with alcohol and treated with ammonia, which dissolves the tungstic acid, leaving the silicic and niobic acids undissolved. These are filtered off, and the filtrate is evaporated and ignited, whereby pure tungstic acid is obtained.

Another method is to fuse 6 parts of the finely powdered mineral with 4 parts of carbonate and 1 part of nitrate of potash in a platinum crucible, by which process the tungstic acid is entirely converted into tungstate of potash, which is dissolved out by water and separated by filtration from the insoluble oxides. The filtrate is nearly neutralized with nitric acid and precipitated by subnitrate of mercury, a few drops of ammonia being added to neutralize the nitric acid. The precipitate is thoroughly washed, first with water, and lastly with a very dilute solution of subnitrate of mercury, and ignited, whereby anhydrous tungstic acid is obtained. Insoluble tungstates may also be decomposed by heating with concentrated sulphuric acid, or by fusion with bisulphate of potash.*

If the ore contains tin as well as tungsten, the tungstic acid

* Conington's Handbook of Chemical Analysis, p. 105.

separated by either of these methods will be mixed with binoxide of tin (stannic acid). In that case, a weighed quantity of the mixture of tungstic acid and oxide of tin must be heated to redness in a porcelain crucible, having a hole in its lid, through which a stream of dry hydrogen is passed on to the ignited mass. The tin is thereby reduced to the metallic state, and the greater part of the tungstic acid (WO^3) is reduced to binoxide of tungsten (WO^2). The contents of the crucible are then boiled with hydrochloric acid, which dissolves the tin and leaves the oxide of tungsten, which may then be reconverted into tungstic acid by ignition in the air and weighed. (W. P. Dexter.*)

ANALYSES OF TUNGSTEN ORES.

Wolfram is a neutral tungstate of iron and manganese, in which the numbers of equivalents of protoxide of iron and protoxide of manganese are together equal to the number of equivalents of tungstic acid. The proportion of tungstic acid in pure specimens of wolfram is about 76 per cent., but the proportions of iron and manganese vary considerably.

I. $5WO^3$. (2FeO . 3MO).

From Zinnwald.

	Calculated.	Schaffgotsch.[1]		Kussin.[2]		Schneider.[3]	Weidinger.[4]	
$5WO^3$.	76·89	75·99		75·89	75·92	75·90	76·01	75·62
2FeO .	9·30	9·62	9·52	9·63	9·38	9·40	9·81	8·73
3MnO .	13·81	13·96	13·28	13·60	14·04	13·86	13·90	12·17
CuO . .		0·48					1·19	TiO^2 1·89
								HO 0·31
	100·00	100·05		99·12	99·34	99.16	100·91	98·72

Kerndt.[5]

	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*
$5WO^3$.	76·34	75·62	75·96	75·83	75·47	75·76	75·80	75·68	75·43
2FeO .	9·61	9·54	9·53	9·20	9·53	9·73	9·78	9·56	9·64
3MnO .	14·20	14·85	14·49	15·56	14·26	14·49	14·41	14·30	14·90
	100·15	100·01	99·98	100·59	99·26	99·98	99·99	99·54	99·97

* Pogg. Ann. xcii. 335.

[1] Gmelin's Handbook (English edition), iii. 295.

[2] Rammelsberg's Handwörterbuch, 3 Suppl. 127.

[3] Journal pr. Chem. xlix. 321; Silliman's Journ. [2] x. 254.

[4] Zeitsch, Pharm. 1855, p. 71.

[5] Journal pr. Chem. xlii. 81.

a and *b* are from Zinnwald; *c* from Lock Fell, Cumberland; *d* from Neubescheert Glück, Freiberg; *e* from Huntingdon, Connecticut; *f* from Trumbul, Connecticut; *g* from Mäuseberg, near Neudorf, in the Harz; *h* from Schlackenwald; *i* from Altenberg.

II. $5WO^3$ (3FeO. 2MnO).

	Calculated.	Vauquelin.[1] *a*
$5WO^3$	76·87	
3FeO	13·95	13·08
2MnO	9·18	10·86
	100·00	

III. $4WO^3$ (3FeO. MnO).

	Calculated.	Berzelius.[1] *b*	Schaffgotsch.[1] *c*
$4WO^3$	76·83	80·52	
3FeO	17·43	17·95	17·50
MnO	5·74	6·05	5·76
	100·00	104·52	

IV. $5WO^3$ (4FeO. MnO).

	Calculated.	Schaffotsch.[1] *a*	*b*	Ebelmen.[1] *c*	Vauquelin.[1] *d*	Schneider.[2] *e*	*f*	Petzold.[6] *g*
$5WO^3$	76·82			76·20		76·04	76·21	76·57
4FeO	18·59	19·16	19·24	19·19	20·77	19·61	18·54	18·98
MnO	4·59	4·74	4·97	4·48	5·75	4·98	5·23	4·90
CuO						0·28	0·40	0·70
MgO				0·80		trace	0·36	trace
	100·00			100·67		100·91	100·74	101·15

	Kerndt. *h*	*i*	*k*	*l*	*m*	*n*
$5WO^3$	75·85	75·64	76·02	75·82	75·90	75·92
4FeO	19·26	19·55	19·20	19·32	19·24	19·35
MnO	4·89	4·80	4·75	4·84	4·80	4·73
	100·00	99·99	99·97	99·98	99·94	100·00

a from Ehrenfriedersdorff; *b* from Monte Video; *c*, *d* from Limoges; *e* from Strassberg, in the Harz; *f* from Neudorff, in the Harz; *g* from Strassberg; *h* from Ehrenfriedersdorff; *i* from Nertschink; *k* from Monte Video; *l* from Chanteloupe; *m* from Harzgerode; *n* from Cumberland.

V. $6WO^3$ (5FeO. MnO).

	Calculated.	Schneider.[2] From the Meiseberg Mines, in the Harz.
$6WO^3$	76·77	76·25
5FeO	19·36	20·27
MnO	3·87	3·96
CaO		0·28
MgO		0·15
	100·00	100·91

[6] Pogg. Ann. xciii. 474.

Dr. Richardson has analysed a specimen of wolfram from Bohemia, in which the proportion of tungstic acid is less than any of the preceding, viz., 73·60 WO^3, 11·20 FeO, and 15·75 MnO (making together, 100·55).

Tungstate of Lead, WO^3. PbO.

	Calculated.	Lampadius.[7]	Kerndt.[8] Fro	Zinnwald.
WO^3	51·58	51·75	51·43	52·03
PbO	48·42	48·25	47·12	44·86
CaO			1·26	1·53
FeO and MnO			0·31	0·63
	100·00	100·00	100·12	99·05

E. J. Chapman[9] has analysed a specimen of native tungstate of lead from Coquimbo, in Chili, which gave 59·50 per cent. and 59·84 per cent. WO^3; 33·26 PbO; and 6·37 lime. The proportion of tungstic acid is about midway between that of a neutral and a bitungstate (68·2 per cent.).

Tungstate of Lime (*Scheelite*), WO^3. CaO.

	Calculated.	Berzelius.[10] Westmanland.	Bucholz & Brandes.[10] Schlackenwalde.	Zinnwald.	Rammelsberg.[11] The Harz.	Carrière.[12] Framont.
WO	80·95	80·42	81·00	76·50	78·64	80·35
CaO	19·05	19·40	19·06	16·50	21·56	19·40
Impurities				5·54		
	100·00	99·82	98·06	98·54	100·20	99·75

CHROMATES OF POTASH AND SODA.

Chromic acid forms several highly coloured salts which are used as pigments. It is also very useful as an oxidizing agent, as it readily gives up half its oxygen to bodies capable of uniting

[7] Gmelin's Handbook (Engl. ed.), v. 167. The locality of the specimen analysed is not given.

[8] J. pr. Chem. xlii. 81.

[9] Phil. Mag. [4], vi. 120.

[10] Gmelin's Handbook (Engl. ed.), iv. 44.

[11] Pogg. Ann. lxxvii. 245.

[12] Jahrb. Miner. 1853, 838.

with that element, being thereby reduced to sesquioxide of chromium:

$$2CrO^3 - O^3 = Cr^2O^3.$$

This property of chromic acid finds numerous applications in the chemical laboratory, in the arts of dyeing and calico printing, and in bleaching tallow, palm-oil, &c. The acid is sometimes used for this purpose in the free state, but more frequently in the form of a salt, bichromate of potash or chromate of lead, for example. When a chromate is mixed with excess of sulphuric acid to set the chromic acid free, and at the same time brought in contact with an oxidable body, such as sulphurous acid, sulphuretted hydrogen, sugar, alcohol, palm-oil, or other organic substance, the chromic acid is decomposed in the manner above mentioned, the reduction being indicated by a change of colour in the liquid, from red or yellow to green, and the liberated oxygen entering into combination with one or more of the elements of the reducing agent.

Chromic acid forms salts containing 1 and 2 equivalents of acid to 1 eq. of base; *e. g.*, chromate and bichromate of potash, $KO.CrO^3$ and $KO.2CrO^3$. According to Graham, there is likewise a terchromate of potash, $KO.3CrO^3$. There are also basic chromates containing 2 eq. of base to 1 eq. of acid; *e. g.*, *subchromate of lead*, $2PbO.CrO^3$.

The chromates of the alkalies are soluble in water and crystallize well. The neutral chromates of magnesia and zinc are likewise soluble. All other neutral chromates are insoluble in water, but soluble in excess of the stronger acids, especially in nitric acid. Such solutions may be regarded as containing acid chromates or bichromates of the several bases: thus, neutral chromate of lime treated with excess of sulphuric acid, yields sulphate of lime, and a solution containing half the lime together with the whole of the chromic acid. The bichromates of baryta and lime may be obtained in the crystalline form.

The neutral chromates of the alkalies are yellow, the bichromates orange-red. *Neutral chromate of potash*, $KO.CrO^3$, crystallizes in oblique prisms, isomorphous with sulphate of potash; 100 parts of water at 10° Fah. dissolve 48⅓ parts of it, and the solution preserves its yellow colour even when largely diluted. *Neutral chromate of soda* forms large fine crystals, containing 10 eq. of water ($NaO.CrO^3+10HO$) and having the form of Glauber salt. These neutral chromates are obtained by heating

chrome-iron ore with the corresponding alkalies in presence of an oxidizing agent. When treated with excess of nitric or sulphuric acid, they yield the bichromates. *Bichromate of potash* ($KO.2CrO^3$), which is the salt most extensively used in the arts, crystallizes in large, rectangular, four-sided tables or prisms of a bright orange-red colour. Water at 60° dissolves $\frac{1}{10}$ of its weight of this salt, and a much larger quantity at the boiling heat. *Bichromate of soda* crystallizes in thin six-sided prisms bevelled at the ends, and of a fine hyacinth-red colour. It is more soluble than the monochromate, and therefore crystallizes after it.

The insoluble chromates are obtained by precipitation from solutions of the alkaline chromates. Most of them are yellow or red. Solutions of the alkaline chromates form light yellow precipitates with baryta and lime-salts; bright yellow with salts of lead, bismuth, and zinc; brick-red with sub-salts of mercury; and brown-purple with silver-salts.

We now proceed to describe the preparation of the chromates of potash and soda, from which, as just observed, all the other chromates are easily obtained. We shall speak particularly of the chromates of potash, as they are the salts most used in the arts.

The most abundant ore of chromium is chrome-iron ore, a compound of protoxide of iron with sesquioxide of chromium, $FeO.Cr^2O^3$. When this mineral is heated with an alkaline nitrate, or with an alkaline hydrate or carbonate, in contact with the air, both its constituent oxides are raised to a higher state of oxidation, the protoxide of iron being converted into sesquinoxide and the oxide of chromium into chromic acid, which unites with the alkali.

The process first adopted for the preparation of chromate of potash was to calcine chrome-iron ore with nitrate of potash. The ore finely pulverized is mixed with half its weight of nitre in rough powder, and the mixture exposed to the heat of a reverberatory furnace for several hours, care being taken to stir it frequently. By subsequent lixiviation with water, a yellow solution of chromate of potash is obtained, from which, by quick evaporation, the neutral chromate ($KO.CrO^3$) is thrown down in yellow crystalline granules; and by redissolving this granular salt in water and leaving the solution to evaporate slowly, the chromate is obtained in regular crystals.

The concentrated solution of the neutral yellow chromate treated with one of the stronger acids—nitric acid is generally

used—yields the bichromate; and by evaporating the solution to the crystallizing point, mechanically separating the crystals of the bichromate from those of the nitrate or other potash-salt formed at the same time, and recrystallizing several times, the bichromate is obtained in large rectangular tables of an orange-red colour.

The process of preparing chromate of potash may be rendered more economical by substituting carbonate of potash (pearlash) for a portion of the nitre, and still more by dispensing with the nitric altogether, and effecting the oxidation by means of air admitted into the reverberatory furnace in which the calcination takes place. The addition of lime is found to facilitate the oxidation.

Mr. Charles Watt, Jun., has shown, that when lime is used the nitrate of potash may be entirely replaced by the sulphate, the decomposition being materially facilitated by the presence of the lime; this substitution effects a great saving in the cost of manufacture. The process is as follows:—The sulphate of potash is ground or otherwise intimately mixed with the pulverized ore, and the lime is then added, being also intimately mixed with the mass. The mixture is then subjected to a strong red heat for about four hours. The nature of the furnace used for this purpose is not of any great importance, so long as carbonaceous matters from the fire are entirely excluded and the required temperature is attained. Unless strong heat is employed, no decomposition takes place; but the temperature required is not greater than that which is necessary when nitrates are used. The mass should be well raked every half hour to ensure that the whole is sufficiently heated. (Pharm. J. Trans. xv. 32.)

Mr. R. A. Tilghmann has patented two processes (Feb. 1st, 1847, No. 11,558), for the preparation of alkaline chromates:—1. To obtain chromate of potash or soda, the chrome ore in powder is mixed with twice its weight of chalk, also in powder, and the mixture is worked into a stiff paste with water. The paste is then made into pellets half an inch in diameter, which, after being thoroughly dried, are placed in a vertical cylindrical retort, together with chloride of potassium or chloride of sodium. At the bottom of the retort, a steam-pipe enters, through which steam at a high temperature is conveyed. There is also another pipe attached to the retort, through which atmospheric air is admitted in quantity sufficient to convert the oxide of chromium

into chromic acid. During the decomposition, hydrochloric acid passes off with the steam, and the alkaline base unites with the chromic acid to form chromate of potash or soda:

$$CrO^2 + 2KCl + 3O + 2HO = 2(KO.CrO^3) + 2HCl$$

The process is complete when the steam which passes off is no longer acid, but merely contains saline particles. The contents of the retort are then withdrawn, and, after cooling, are thrown into cold water, and the chromate is dissolved out and crystallized.

2. In Mr. Tilghmann's second process, the source of the alkali is *felspar* (silicate of alumina and potash), which is heated in an oxidizing atmosphere with lime and chrome-iron ore. The materials are ground to fine powder and mixed in the proportion of 4 parts by weight of felspar, 4 parts of lime or an equivalent quantity of carbonate of lime, and 1 part of chrome ore. The mixture is spread on the hearth of a reverberatory furnace, and kept at a bright red heat from 18 to 20 hours, stirring and turning it over frequently, so that all parts may be equally exposed to heat and air. An oxidizing atmosphere is preserved by the admission of sufficient air into the chamber of the reverberatory furnace. The heat should not be permitted to rise high enough to cause even incipient fusion of the charge, which should be kept in a porous state. When an examination of the charge in the usual manner shows that it contains the proper quantity of alkaline chromate, it is withdrawn from the furnace and lixiviated with water.

Mr. Swindell's process for manufacturing chrome-salts is as follows:—The powdered chrome ore is mixed with its own weight of common salt, chloride of potassium, or hydrate of lime, and the mixture is exposed in a reverberatory furnace to a full red or even a white heat, a jet of very hot steam being passed over the mass while in a state of fusion, and the mixture well stirred every ten or fifteen minutes. When the usual method of testing shows the process to be finished, the resulting compound is found to consist of chromate of soda, potash, or lime, the chloride and the iron having passed off in the form of sesquichloride of iron. (Chem. Gaz. 1851, p. 419.)

Mr. James C. Booth, of Philadelphia, has patented a process (9th November, 1852, No. 690) for preparing chromate of potash, by which the oxidation of the chromic oxide is considerably accelerated. In the ordinary mode of preparation, by heating the chrome-iron ore with carbonate of potash, either with or without

nitre, a considerable portion of oxygen is employed in converting the protoxide of iron into sesquioxide; consequently, only a portion of the chrome oxide becomes converted into chromic acid at one operation; and to complete the process, the heating with potash must be repeated several times, which involves a considerable loss of potash by volatilization. Now, in Mr. Booth's process, the iron is first reduced to the metallic state by heating the ore with carbon in any of its forms, or with carbonic oxide or carburetted hydrogen, and then removed by digesting the mass with dilute sulphuric acid. The residual chromic oxide is then heated with carbonate of potash in the usual way, and is at once converted into chromate of potash. The production of sulphate of iron incidental to this process also assists in defraying the expense. The mode of carrying out the process is as follows:—Chrome-iron ore ground to powder by the usual mechanical means, is mixed with about $\frac{1}{3}$ of its weight of powdered charcoal, coke, anthracite or bituminous coal, and the mixture is placed upon the hearth of a reverberatory furnace, constructed like the reverberatory furnaces for reheating or puddling iron, so that the heat or flame may be as free as practicable from uncombined oxygen or atmospheric air. By this operation, the greater part or all of the oxide of iron in the chrome ore will be decomposed, and the iron reduced to the metallic state. When one charge of the mixture has been reduced as above described, it is to be raked out, and a second charge introduced into the heated furnace, reduced in its turn, and replaced by a third charge, and so on. Each charge when raked out of the furnace is thrown into vats containing dilute sulphuric acid, whereby the iron is dissolved, and a solution of proto-sulphate of iron or copperas is thereby formed. This solution (still containing free acid) is to be drawn off, and run upon a fresh charge of reduced ore, in order more fully to saturate the free acid, after which it is again to be drawn off and evaporated to crystallization, so as to produce copperas in a state adapted for commerce. The residue in the vats is then to be well washed with water, and dried, and afterwards mixed with carbonate of potash, or with carbonate of potash and saltpetre, and heated in the usual way.

The quantity of oil of vitriol used in the process is nearly equal in weight to $\frac{2}{3}$ of that of the ore.

The washings of the ore containing sulphate of iron may be economically used for diluting the acid which is to be applied to remove the iron from a succeeding charge.

Jacquelain prepares bichromate of lime from chrome-iron ore, and converts that salt into bichromate of potash by double decomposition; a method which is found to be more economical than the direct preparation of the potash-salt from the ore.

The chrome ore, after being ground to very fine powder and sifted, is mixed with chalk in rotating barrels, and the mixture is spread in a layer 1½ to 2 inches thick on the hearth of a reverberatory furnace, heated to bright redness, for 9 or 10 hours, and stirred at least every hour. After this treatment, the mixture has a yellowish green colour, dissolves in hydrochloric acid, and, with the exception of a certain quantity of sand, consists essentially of *neutral chromate of lime* ($CaO . CrO^3$), mixed with oxide of iron. This mass is ground to powder by millstones; the powder is stirred up with hot water, and sulphuric acid is added till a slight acid reaction becomes apparent. The neutral chromate of lime is thereby converted into *bichromate*. The liquid also contains sulphate of iron, which is precipitated in the same vessel by stirring up with chalk, which does not affect the chrome-salt. The precipitate having settled down, the clear solution of bichromate of lime containing a little sulphate is run off, and may be used without further treatment for preparing by double decomposition bichromate of potash, chromate of lead, either neutral or basic, and chromate of zinc. To obtain bichromate of potash, the solution of bichromate of lime is treated with carbonate of potash, which throws down carbonate of lime in a form easy to wash, leaving bichromate of potash in solution, which may then be evaporated and crystallized.

The following are said to be the practical advantages of this process as compared with the old method of obtaining bichromate of potash:—1. The necessity of looking continually after the workmen is avoided, and the frequent renewal of the surface of the material by means of rakes is not required; this continual stirring being necessary in the old process to bring the chrome ore in contact with the oxygen of the air, its greater density causing it to remain at the bottom of the potash-salt in fusion. 2. The rapid wear and tear of the floor of the furnace is avoided. It is true that the simultaneous use of potash and lime now adopted in some works—or, what is still better, the use of lime, saltpetre, and oxide of manganese—tends considerably to facilitate the admixture of the ingredients in the furnace, and thus to prevent the rapid wear and tear to which the floor of the furnace was subjected.

But both these processes afford mixtures of a pasty consistence, and the air can act only on the surface of the agglomerated particles. In the new process, the floor of the furnace undergoes no material wear. 3. Whichever mixture was adopted, there was always a loss of 8 or 9 per cent. of potash at a bright red heat. With the use of chalk no loss of this kind occurs. 4. The loss of potash in the state of silicate was still greater, and the presence of silica was a great impediment to crystallization. 5. The difficulty of knowing when to stop in the conversion of the neutral chromate into bichromate is avoided. If too much sulphuri cacid be added to a solution of neutral chromate of potash, chromic acid is set at liberty, and, during the concentration of the liquors, any organic matter that may be contained in them burns at the expense of the oxygen of the chromic acid, whence results a green uncrystallized sulphate of chromium, which gives a brown colour to the bichromate of potash, insomuch that it is necessary to evaporate the liquid to dryness and calcine the entire mass afresh. All these difficulties are got rid of by the adoption of the new process. 6. M. Jacquelain insists particularly on the necessity of the extreme division of the chrome ore, inasmuch as incomplete pulverization retards the chemical action and consequently increases the consumption of fuel. For this reason it is advisable to levigate the powder and dry it by means of the waste heat of the furnace. (Ann. Ch. Phys. [3], xxi. 478.)

Adulteration of Bichromate of Potash.—A mixture of sulphate of soda and chloride of sodium, coloured with a strong solution of chrome, has been offered for sale as the genuine article. To detect this adulteration, the quantity of moisture in the sample must first be ascertained by weighing out a certain portion and drying it on a sand-bath, and again weighing: the loss of weight will give the quantity of water. The salt is then to be dissolved in distilled water and a soluble salt of lead added till it ceases to give a precipitate. The mass is then to be boiled and more distilled water added; the supernatant liquor is next poured off, and if the sample under examination contains any chloride of sodium, small shining crystalline needles of chloride of lead will form in the liquor as it cools. The remaining precipitate is then to be treated with strong nitric acid, which will decompose the chromate. By adding distilled water, the nitrate of lead formed by the decomposition of the chromate will be dissolved, and the remaining sulphate of lead, if any, may be dried, and its weight ascertained, from which the quantity of sulphate in the

chromate may be calculated. The quantity of chloride may be ascertained, if required, by redissolving the chloride of lead in boiling water, and precipitating with nitrate of silver.

Another method of ascertaining the presence of sulphates and chlorides in bichromate of potash, is to add a large excess of tartaric acid, which will decompose the chromate, forming an amethyst-coloured solution, which, if pure, will give no precipitate with nitrate of baryta or nitrate of silver.

Chromic acid in the free state is used as an oxidizing agent in the chemical laboratory and in manufacturing processes. It forms needle-shaped crystals of a deep crimson colour and very soluble in water. The solution bleaches organic colouring matters.

Chromic acid is prepared on the large scale by decomposing chromate of lead or bichromate of potash with sulphuric acid; but when thus produced, it always contains sulphuric acid, even when an excess of chromate of lead has been used; and when prepared with bichromate of potash, it is necessarily mixed with a considerable quantity of sulphate of potash. These impurities are seldom of any importance when the acid is to be used for manufacturing purposes; but for use in the chemical laboratory a pure preparation must be obtained.

Mr. C. Watt treats chromate of baryta with a large excess of strong nitric acid. The nitrate of baryta thereby produced being quite insoluble in the strong nitric acid, and forming a heavy crystalline precipitate, the chromic acid is easily separated from it by decantration or filtration through asbestos. It must not be allowed to come in contact with any organic matter, or it will be immediately decomposed. The solution is then to be evaporated to dryness, when the nitric acid will be volatilized, leaving pure chromic acid. When the quantity of material operated upon is large, the nitric acid which passes off should be collected in a suitable condensing apparatus, so that it may be used over again. The solution of chromic acid should be tested previous to filtration to see whether it contains any nitrate of baryta; for this purpose a sample of it must be diluted with a considerable quantity of water, and a drop of sulphuric acid added. If any precipitate appears, more nitric acid must be added to the liquid. The only precautions necessary to ensure the purity of the chromic acid prepared by this process are that the nitric acid be pure, strong, and used in considerable excess.

Bolley (Ann. Ch. Pharm. lvi. 113) prepares chromic acid by dissolving a weighed quantity of bichromate of potash in a small quantity of boiling water, and adding to the hot solution the exact quantity of sulphuric acid required to convert the potash into bisulphate. The mixture, when left to cool, solidifies for the most part into a red granular mass consisting of bisulphate of potash with adhering chromic acid. The mixture is stirred to cause the granular mass to subside, the solution is decanted, and the residual bisulphate is washed several times with cold water. There then remains an orange-coloured sulphate of potash with very little chromic acid, the greater part of that acid being contained in the united solutions. The separation thus effected depends upon the circumstance that bisulphate of potash, which dissolves very freely in boiling water (2 parts of the salt to 1 part of water), is but sparingly soluble at ordinary temperatures, and cold water removes sulphuric acid from it with scarcely any potash, leaving neutral sulphate of potash, while the chromic acid dissolves in the cold water. The solution of chromic acid containing only a small quantity of bisulphate of potash is then further concentrated, and the chromic acid is precipitated by adding about an equal volume of strong sulphuric acid, which throws it down free from any trace of bisulphate.

VALUATION OF CHROME ORES.

The value of a chrome ore depends upon the quantity of chromic acid that it will yield. To ascertain this point, it is necessary first to decompose the ore, and obtain the whole of the chromium in the form of a soluble chromate, by methods similar in principle to those which are adopted in the process of manufacturing chromates. In this, as in the manufacturing process, it is much better to calcine the ore with lime, or with a mixture of lime and potash or soda, than with alkali alone, because in the latter case the mixture fuses, and the chrome ore, by its greater specific gravity, sinks to the bottom of the crucible, and does not come in contact with the air.

Professor Calvert, of Manchester, has given two processes* for the analysis of chrome ores. 1. The ore, in fine powder, is mixed with 3 or 4 times its weight of soda-lime (obtained by slaking quicklime with caustic soda, and then drying and cal-

* Quarterly Journal of the Chemical Society, v. 194.

cining the mass), and to this mixture of soda-lime and ore is added one fourth part of nitrate of soda. The whole is then well calcined for two hours, care being taken to stir the pasty mass every quarter of an hour with a platinum wire. This mixture not becoming fluid, the ore is constantly kept in contact with the oxygen of the atmosphere, and thus the oxide of chromium is converted into chromic acid. One treatment is generally sufficient for the complete decomposition of the ore, whereas by the ordinary method of fusing with alkali alone, five or six calcinations are required.

The greater part of the mass is now dissolved in water, and the insoluble portion treated with sulphuric acid diluted with twice its bulk of water; the whole is then removed from the crucible, and a little alcohol is added to the solution in order to render the sulphate of lime insoluble. The whole is next thrown on a filter and washed with weak alcohol, which dissolves all the bichromate formed, and leaves the sulphate of lime together with any portion of ore that may not have been attacked. The sulphate of lime may be removed by washing the filter with boiling water, and the residual ore, if any, is to be recalcined.

The solution containing the bichromate of soda is now neutralized with ammonia, and oxalate of ammonia is added, which gives rise to a small precipitate of sesquioxide of iron, alumina, and oxalate of lime, together with a little silica dissolved by the sulphuric acid. The precipitate having been separated and well washed, the liquor is either mixed with alcohol to reduce the chromic acid to the state of sesquioxide, which may then be precipitated, washed, dried, ignited, and weighed; or, better, the liquor is rendered acid, and the amount of chromic acid estimated by Dr. Penny's process* with protochloride of tin. This method depends on the reaction of protochloride of tin with bichromate of soda or potash in presence of free hydrochloric acid, whereby the protochloride of tin is converted into bichloride, and the chromic acid into sesquichloride of chromium:

$$3SnCl + NaO.2CrO^3 + 7HCl = 3SnCl^2 + NaCl + 7HO + Cr^2Cl^3.$$

A solution of protochloride of tin of known strength† is added to the solution of bichromate of soda, till the latter is completely

* Chem. Soc. Qu. J. iv. 239.

† The strength of a solution of protochloride of tin is most easily ascertained by means of a standard solution of pure bichromate of potash.

decomposed,—which may be known by the solution no longer giving a yellow precipitate with acetate of lead—and the quantity of bichromate present is calculated from the amount of tin in the solution used. Penny has shown, by direct experiment, that in the above reaction, 100 parts of metallic tin correspond to 83·2 parts of bichromate of potash (or 78·4 parts of bichromate of soda).

2. Another method of decomposing chrome ore, proposed by Professor Calvert, is to calcine the finely divided ore with nitrate of baryta. A small quantity of caustic potash added towards the end of the operation facilitates the action, and gives rise to chromate of potash. The pasty condition of the fused baryta prevents the ore from falling to the bottom, and thus keeps it in contact with the air. On cooling, the crucible and its contents are immersed in dilute nitric acid, which dissolves the greater portion of the mass, leaving the unattacked ore, which, after being washed, may be recalcined. The liquor containing the bichromates of potash and baryta, nitrate of baryta, sesquioxide of iron, alumina, and lime, is first heated with sulphate of potash, to precipitate the baryta as sulphate, which is collected on a filter and washed; ammonia and oxalate of ammonia are then added to throw down sesquioxide of iron, alumina, and lime; the mixed precipitate is collected and washed, and the amount of chromic acid determined as before.

ANALYSES OF CHROME-IRON ORE.

	Abich.		Berthier.	Heybert.		Laugier.		Klaproth.
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*
Sesquioxide of Chromium	60·04	54·92	51·6	39·51	51·56	53	54·08	55·5
Alumina . .	11·77	13·23	10·0	13·00	9·72	11	9·02	6·0
Protoxide of Iron	20·13	18·97	35·0	36 00	35·14	34	25·66	33·0
Magnesia . .	7·52	9·69	—	—	—	1	5·36	—
Protoxide of Manganese	—	—	—	—	—	—	—	—
Silica . . .	0·36	0·83	3·0	10·60	2·90	1	4·83	2·0
Water . . .	—	—	—	—	—	—	—	2·0
	99·82	97·64	99·6	99·11	99·32	100	98·95	98·5

a is crystallized: *b* massive chrome-iron ore, from Baltimore; *c*, *d* also from Baltimore; *e* from Pennsylvania; *f* from Siberia; *g* from Rocraas; *h* from Krieglach. (Gmelin's Handbook, English edition, v. 299.)

	Moberg.[1]	Rivot.[2]	Landerer.[3]		Garret.[4]	Starr. Garret.[4]	Bechi.[5]	
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*
Sesquioxide of Chromium	64·17	63·37	42·00	54·00	63·38	60·83	41·55	42·13
Alumina . .	10·83	1·96	16·00	18·00	—	0·92	—	19·83
Sesquioxide of Iron	—	30·04	—	—	38·66	38·95	62·02	—
Protoxide of Iron	18·42	—	34·00	20·00	—	—	—	33·93
Protoxide of Nickel	—	—	—	—	2·28	0·10	—	—
Magnesia . .	6·68		5·00	8·00	—	—	—	—
Lime	—	2·02	—	—	—	—	—	—
Silica, or Titanic Acid	0·91	2·21	—	—	—	0·61	1·25	4·75
	101·01	99·60	97·00	100·00	104·32	101·41	104·82	100·64

a from Beresow (previously digested with hydrochloric acid); *b* from Baltimore; *c* from Ihami; *d* from Scyros; *e* from Chester county, Pennsylvania; *f* chrome-iron sand from the same locality; *g* the same freed from magnetic particles; *h* from Volterra, in Tuscany.

SILICATES OF POTASH AND SODA.

SOLUBLE GLASS—WATER-GLASS.

Silica or silicic acid is one of the most widely diffused of all mineral substances. In the free state, either pure or mixed with small quantities of other substances, it occurs in the form of rock-crystal, sand, and flint; and in combination with potash, soda, lime, magnesia, alumina, and other metallic oxides, it forms an immense number of minerals, which, either separately or aggregated in groups, constitute a very large proportion of the crust of the earth,—granite, porphyry, slate in all its varieties, and the numerous clays resulting from the decomposition of these

(1) Journ. für praktische Chemie. xliii. 14.
(2) Ann. Ch. Phys. [3], xxx. 202.
(3) Jahrb. Miner. 1850, 682.
(4) Silliman's Journ. [2], xiv. 45.
(5) *Ibid*, 62.

rocks, all consisting of silicious minerals. Now, silica, as it occurs in nature in the free state, and in most of its combinations, is perfectly insoluble in water, and resists the action of all acids except hydrofluoric acid. Indeed, it is only the potash and soda salts of silicic acid, in which the proportion of alkali is considerable, that are soluble in water; when the silica is in excess, even these alkaline silicates become insoluble.

The soluble silicates of potash and soda possess many properties, which render them of great importance both in the economy of nature and for various applications in the arts; and their preparation and uses have of late years occupied the attention of several manufacturing chemists.

The first attempt to prepare the soluble silicates on the large scale, and apply them to economical use, appears to have been made by Fuchs, of Munich, who, in the year 1825, published a paper on "Water-glass," in Kastner's Archives of Natural Philosophy, vol. v. pp. 385—412.* This paper describes the preparation of potash and soda water-glass, and various applications thereof to the solidification of stone and porous earthenware, but chiefly to a new method of painting with mineral colours, called "Stereochromy."

Considerable extension has been given to the application of water-glass for these purposes, especially for the production of cements and the hardening of stones for building, by the researches of Professor Kuhlmann, of Lille, contained in a series of papers read before the French Academy of Sciences in the years 1841 to 1857.†

While these researches were in progress on the Continent, Mr. Frederick Ransome, of Ipswich, was also pursuing experi-

* Separately printed by Leonhard Schrag, of Nuremberg, with the title, "On a new product from Silica and Potash:" by Johann Nep. Fuchs, Professor of Mineralogy. A translation of this paper, made by desire of His Royal Highness the Prince Consort, is published in the Journal of the Society of Arts, vol. vii. (1859,) pp. 521—532.

† These researches have been collectively published in a pamphlet, entitled "*Silicatisation, ou application des silicates alcalins solubles au durcissement des pierres poreuses, &c.:*" par M. Fréd. Kuhlmann, 3me. édition. Paris: Victor Masson, 1858. 8vo. [Attached to this pamphlet is the Report of a French Government Commission on M. Kuhlmann's researches, which has also been translated into English by desire of the Prince Consort. The translation is given in the Journal of the Society of Arts, vol. vii. p. 584, together with that of M. Kuhlmann's "Practical Instructions on the use of the Soluble Alkaline Silicates."]

ments on the alkaline silicates, chiefly with a view to the preparation and preservation of building-stones. His first patent for producing a compact stone by cementing particles of sand, waste fragments of stone, &c., by means of soluble silicates, bears date the 22nd of October, 1844. Several other patents for similar purposes have since been taken out by Mr. Ransome and others.

The soluble silicates are produced by igniting sand, pulverized quartz, flint, or other forms of silica, with the hydrates of potash and soda, or with the carbonates, nitrates, or other salts of those bases containing volatile acids. When 1 part of silica is fused with $2\frac{1}{4}$ parts of carbonate of potash, or with $1\frac{2}{4}$ parts of anhydrous carbonate of soda, the product is a transparent glass, consisting of *monosilicate of potash* or *soda* (KO or NaO).SiO^2. It deliquesces in the air, and dissolves readily in water, forming a solution commonly called *liquor silicum*. When a strong solution of this monosilicate is treated with hydrochloric or nitric acid, the greater part of the silica is precipitated in gelatinous flakes, a certain quantity, however, always remaining dissolved. But if the solution of the silicate be largely diluted with water, and a quantity of hydrochloric acid added sufficient to give it a strong acid reaction, no precipitate is formed, but the silica remains dissolved. In this state, then, it appears that silica is soluble in dilute acids. If, on the other hand, the gelatinous silica, precipitated as above, be dried and heated to redness, it becomes completely insoluble in acids, whether strong or dilute. Silica in the gelatinous state dissolves readily in caustic alkalies at ordinary temperatures; and even after ignition it dissolves in alkalies on boiling, especially under increased pressure.

The compounds to which the term *water-glass* is more especially applied contain a larger proportion of silica. Fuchs's *potash water-glass* is a *tetrasilicate*, $KO.4SiO^2$; and his *soda water-glass*, a $\frac{4}{5}$-silicate, $2NaO.5SiO^2$. These compounds dissolve slowly in cold, readily in boiling, water. The characters of the solutions resemble those of the liquor silicum, excepting that the silica, being in larger proportion, is more readily precipitated. We proceed to describe the preparation in detail.

PREPARATION OF WATER-GLASS.

Fuchs's Method.—1. To prepare *potash water-glass*, a mixture of 15 parts of pulverized quartz or quartz-sand, 10 parts of well-purified pearl-ash, and 1 part of powdered charcoal (to decompose and expel the sulphuric acid in the pearl-ash) is ignited for five or six hours at a temperature about equal to that required to melt common glass, then left to cool, broken up, pulverized, and boiled with 5 times its weight of water in an iron pot for three or four hours, the water being replaced as it evaporates. The vitreous product then dissolves slowly, but completely, with the exception of a small gelatinous residue arising from impurities. After the whole is dissolved, the boiling is continued so as to concentrate the solution to a specific gravity of 1·24 to 1·26. In this state it is sufficiently liquid to be used in many operations; in some cases it requires to be diluted with water when evaporated, and for some purposes it may be evaporated to a syrupy consistence.

Water-glass thus prepared is often contaminated with a small quantity of sulphide of potassium, arising from the deoxidation of sulphate of potash by the charcoal. To decompose this sulphide a small quantity of oxide of copper, or litharge, must be added towards the end of the boiling. The sulphide of potassium is thereby converted into potash, a certain excess of which renders the glass more applicable for many purposes. If, however, a perfectly neutral water-glass is required, the neutrality may be ensured by boiling the liquid with freshly precipitated silica as long as any is taken up. If litharge is used to decompose the sulphide of potassium, care must be taken not to add too much, since an excess causes the glass to coagulate.

After purification in the manner just described, the solution is left to cool and clarify, the vessel being well closed to prevent access of air, the carbonic acid in which would decompose the soluble silicate. The clear liquid is then decanted from the deposit (which makes a good manure), and stored in carboys. It may also be evaporated to a jelly, and packed in tinned iron vessels.

Water-glass may likewise be obtained in the solid state by mixing the concentrated solution with one-fourth of its volume of rectified spirits of wine; a gelatinous precipitate is thereby

produced, which contracts strongly after a few days, and is deposited in the bottom in a solid mass; and, if the supernatant liquid, which often contains a little carbonate of potash, with traces of chloride of potassium, chloride of sodium, and sulphide of potassium, be decanted, and the deposit slightly washed with cold water and squeezed, the water-glass is obtained in the solid state very pure, and completely saturated with silica. Water dissolves it easily and completely.

2. *Soda water-glass* is prepared in the same way as the potash glass; but, as the saturating power of soda is greater than that of potash, a smaller quantity of it suffices for a given quantity of quartz. The proportions are 45 lbs. of quartz, 23 lbs. of anhydrous carbonate of soda, and 3 lbs. of charcoal. The mixture fuses somewhat more readily than the potash glass. According to Buchner, soda water-glass may be prepared more cheaply by means of sulphate of soda, in the proportion of 100 parts quartz, 60 anhydrous sulphate of soda, and 15 to 20 charcoal-dust.

When the mass is completely saturated with silica, it gives with water a somewhat more opaque liquid than the glass prepared from potash in a like state of concentration.

Rectified spirit does not precipitate it completely like the potash water-glass, merely converting it into a gelatinous mass, and giving no precipitate at all, or only after a short time, when it is not completely saturated with silica, or when slightly diluted.

Double Water-glass.—Potash and soda water-glass are miscible in all proportions; but the normal double water-glass, which contains potash and soda in equivalent proportions, may be obtained by fusing together 100 parts of quartz and 121 parts of Rochelle salt (tartrate of potash and soda). This process is, however, too expensive for practical purposes. A cheaper mode of preparation is to fuse a mixture of nitrate of potash and nitrate of soda in equivalent proportions with the corresponding amount of quartz; or, again, 100 parts of quartz, 28 pearl-ash, 22 anhydrous carbonate of soda, and 6 powdered charcoal. This mixture fuses much more readily than any of the preceding. A solution of double water-glass, suitable for all practical applications, may also be prepared by mixing 3 measures of concentrated potash water-glass with 2 measures of concentrated soda water-glass.

Fixing Water-glass.—We have already observed that one of the applications of water-glass is to the preparation of colours for mural painting. Now, paintings executed in this manner require to be *fixed* by washing them with a solution of water-glass. For this purpose it is found that water-glass saturated with silica is not well adapted, inasmuch it undergoes rapid decomposition when exposed to the air, depositing an opaque film of silica, which gives the pictures a cloudy and dirty appearance. This inconvenience is obviated by using a solution prepared by mixing water-glass, saturated with silica, with a solution of monosilicate of soda (*liquor silicum*), obtained by fusing 2 parts of powdered quartz with 3 parts of anhydrous carbonate of soda. One measure of this concentrated *liquor silicum*, added to four or five measures of concentrated water-glass saturated with silica, forms a solution well adapted for fixing colours. (Fuchs.)

The preceding descriptions include all that is essential in the preparation of water-glass. Various modifications in the process have, however, been introduced to facilitate the preparation on the large scale, or to render the product better adapted for particular purposes.

Kuhlmann heats 1 part of carbonate of potash with 1, 1½, or 2 parts of silica in a reverboratory furnace for six or seven hours, till complete fusion is effected. If the product contains sulphides, which would interfere with its use in the preparation of colours, it may be purified by fusion with a small quantity of nitre.

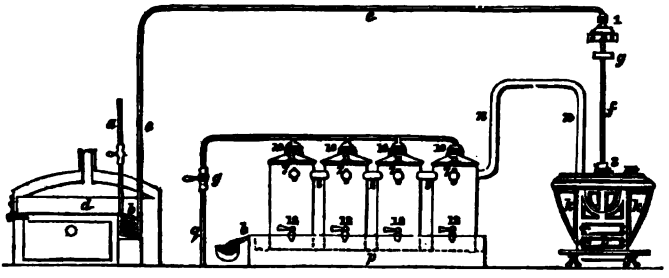
Soluble silicates may also be prepared by boiling silica with solutions of caustic alkalies under pressure. This mode of preparation is practised by Mr. Ransome, and also by M. Kuhlmann.

The preparation of water-glass by boiling silica in caustic alkali under pressure was first patented in England by Mr. Ransome in 1844. This process, with which that of M. Kuhlmann is almost identical, is as follows: 100 lbs. of crystallized carbonate of soda or 50 lbs. of carbonate of potash (pearl-ash) are dissolved in about 50 gallons of water, and the solution, after being rendered caustic by means of lime, is reduced to the bulk of 20 or 25 gallons by heat. This caustic alkaline lye is then put, together with 100 lbs. of finely broken flints or other convenient silicious substance, into an iron boiler or digester, and the mixture is heated, with frequent agitation, for 10 or 12 hours up to

a pressure of about 60 lbs. to the square inch. When the mixture is sufficiently incorporated, it may be removed from the boiler and passed through a sieve to separate any undissolved stone. It is then fit for use; or it may be tempered to any required consistency by the admixture of sand or finely powdered flint. If too thick for use, it may be diluted with water.

A peculiar apparatus for preparing soluble silicates in this manner has been patented by Mr. Harris Hardinge, of New York (24th December, 1853, No. 2991). It is represented in the following diagrams, Fig. 15 being a side elevation of the

FIG. 15.



whole apparatus, and Fig. 16 a vertical section of the dissolving boiler.

FIG. 16.

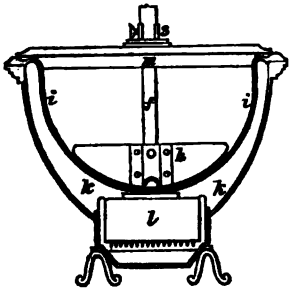


FIG. 17.

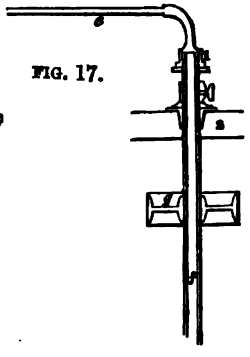
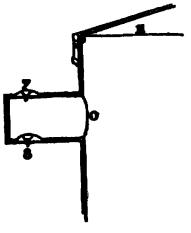


FIG. 18.



a is a pipe and cock leading from any ordinary steam boiler, and connecting to a coiled pipe *b*, in a furnace *d*, the fire being built within the coiled pipe as at *c*. This furnace has a damper, and chamber to receive carbonic acid from the charcoal burnt in the furnace *c*, for a purpose hereafter explained. By means of the fire at *c*, the steam in the coiled pipe *b* is raised to a very high temperature, and passes by a pipe *e* into the dissolving boiler *k*.

f is a hollow spindle fitted with a pulley, by which it is rotated, and sustained by a bearing 2 (Fig. 17), and is connected to the pipe *c* by a coupling 1, so as to allow it to rotate. It is supported near its lower end by the collar 3, resting on the cross piece *m* over the top of the boiler *k*, the interior pan of which is shown at *i*. The boiler *k* is heated by fire placed in the fireplace *l*. The spindle *f* extends nearly to the bottom of the boiler *k*, not, however, touching it, and on one side is an opening 4, to enable the steam conveyed by the pipe *e* to pass into the boiler. To the bottom of the spindle *f* is attached a scraper *h*, made to the shape of the boiler *i*, and moving with the spindle, by means of which the ingredients in the boiler are kept in constant motion. The boiler is fitted with a cover *m*, to confine the steam, but it can be raised on one side when necessary. By means of the pipe *n*, the steam from the boiler passes into one or more reservoirs *o*, *o*, standing in a trough *p*, and kept cool by water from a pipe *q*, regulated by the cock 9, through perforated sprinklers 10, the waste water in the trough *p* passing off by an over-flow pipe 6. These reservoirs or condensers are connected together by pipes 5, and are provided with covers 11, secured in any convenient manner, and have cocks 12, by which the condensed liquid is drawn off; they are also fitted with safety valves (see Fig. 18), one, 7, opening outward, and another, 8, opening inward, so as to prevent collapsing or bursting, no pressure being necessary in them.

Finely pulverized quartz saturated with a small quantity of water is put into the boiler *k*, together with a small amount of the usual solvents, as boracic acid,* carbonate of soda, and salts and alkalies of a similar nature, and the mixture is submitted to mechanical agitation by the rotation of the spindle *f* and scraper *h*. Heat is applied in the furnace *l*, as may be necessary, and steam, heated as desired, is supplied by the pipe *e* and spindle *f*, by the combined operation of which the quartz is dissolved in about three hours, with very little addition of the usual solvents. The steam which passes off by the pipe *n*, carries with it very minute particles or capsules of the solution of quartz; and these, condensing in the reservoirs *o*, *o*, form a liquid solution of quartz,

* Silica does not dissolve in boracic acid, even in the state of fusion. Probably the impure commercial acid was used, and the solution of the silica was due to the alkali contained therein. (EDS.)

in addition to that formed in the boiler *k*, thus saving what would otherwise be wasted in the process.

PROPERTIES OF WATER-GLASS.

Solid or fused water-glass, when pure, has the appearance of ordinary glass, and dissolves gradually but completely in boiling water; in the cold, the solution proceeds so slowly that the glass appears almost insoluble. It becomes entirely insoluble only when the proportion of silica is considerably increased. A concentrated solution containing 28 per cent. of anhydrous water-glass is syrupy, tenacious, somewhat turbid, and has a density of 1·25. On boiling, or on exposure to the air, it becomes covered with a tough skin, which disappears when thrust beneath the liquid. After evaporation at a high temperature, it becomes very tenacious, and may be drawn out into threads like melted glass. Acids—even carbonic acid—decompose the solution, and separate silica in the gelatinous form. Solid water-glass is also readily acted upon by dilute acids, and silica is separated in the form of powder.

The solution exposed to the air in open vessels attracts carbonic acid, and suffers decomposition, which causes it to coagulate sooner or later, and gradually produces a slimy deposit, consisting of silica combined with a small quantity of potash; heat accelerates the decomposition. If the liquid is evaporated, and the dry mass rendered anhydrous by further heating, it swells considerably, and is then almost entirely decomposed. Water no longer dissolves it, and acids produce strong effervescence. By calcination, it is brought back to its original state, the silica recombining with the alkali, and the compound again becoming perfectly soluble in water. When a solution of water-glass is to be evaporated to dryness, it is necessary to keep the liquid constantly boiling, in order to prevent the access of carbonic acid. The same precaution must be observed when fused water-glass is to be dissolved; care must also be taken to add the water in the boiling state, so as not to interrupt the ebullition.

When a concentrated solution of water-glass is brushed upon a solid substance, such as glass, marble, or paper, which it does not penetrate, it soon dries up and forms a shining transparent coating, which, however, does not keep long, but becomes gradually dull, opaque, and sometimes cracked, and of a somewhat

pulverulent appearance. This change is due partly to the decomposition just mentioned, partly to loss of water, which air-dried water-glass retains to the amount of about 12 per cent., and loses but slowly, contracting at the same time, and acquiring considerable hardness.

The *alkaline carbonates* and *chlorides*, especially sal-ammoniac, added to a solution of water-glass, precipitate the silica. Sal-ammoniac precipitates a dilute solution gradually, a concentrated solution immediately, converting it into a tenacious mass. The precipitate is pasty at first, and, after long-continued washing, leaves pure silica. *Baryta, strontia, lime, alumina*, and *oxide of lead*, decompose water-glass, removing the whole of the silica and a portion of the alkali in the form of an insoluble double silicate. Nearly all the soluble salts of the earths and heavy metallic oxides likewise produce precipitates, consisting of double silicates.

Phosphate of alumina, and *carbonate, phosphate*, or *sulphate of lead*, triturated with a solution of water-glass, yield a tenacious mass, which, when exposed to the air, becomes as hard as stone. Phosphate of lime is not decomposed by it. *Alcohol*, even in small quantity, precipitates water-glass from its aqueous solution, and thus affords the means of purifying it from the soluble salts of potash or soda. (Fuchs.)

According to the observations of Forchhammer, however, the alcohol—even in the act of precipitation, and still more during the subsequent washing,—withdraws a portion of the alkali, till the residue consists of octosilicate of potash $KO . 8SiO^2$, which is not completely soluble in water.

COMPOSITION OF WATER-GLASS.

	a	*b*	*c*
Water . . .	65·829	38·66	·689
Silica . . .	22·258	44·64	63·600
Soda . . .	11·178	16·25	—
Potash . . .	—	—	34·400

a Soda water-glass from the manufactory of Seibel in Liesing; *b* soda water-glass from Munich; *c* potash water-glass from Kuhlmann's manufactory.

USES OF WATER-GLASS.

I. *For Hardening and Preserving Stones, Preparing Artificial Stone, Cement, &c.*

One of the most important properties of water-glass is its binding or cementing power, by virtue of which it may be applied in various ways for imparting solidit to loose structures, for joining separate parts of bodies or loose articles into a compact mass, or for filling up cracks or fissures.

This effect is sometimes due to a chemical action taking place between the elements of the glass and those of the porous material, in fact, to the formation of a double silicate. Such is the case with magnesia and oxide of zinc; either of these substances ground together with water-glass, forms a mixture which sets after a while into a hard mass; and on boiling this mass with water, only a small quantity of alkali is extracted from it, but no silica.

In many cases, however, the cementing power of the water-glass appears to arise merely from its own gradual decomposition, and the consequent deposition between the particles of the porous material, of a mass of solid silica which binds them together by mechanical adhesion. Phosphate of lime, for example, forms a very compact mass with water-glass, but apparently without any formation of silicate of lime. Mr. Ransome, in 1845, patented a process for the application of a soluble silicate for combining small coal into blocks, and for preserving wood from fire and decay. In this case there could evidently be no chemical action between the water-glass and the porous material.

The action of soluble silicates on limestones is of particular importance. Water-glass sets rapidly when mixed with slaked lime, and slowly dries up to a rather hard mass, consisting of a double silicate of lime and alkali, on which water has no action. With carbonate of lime, also, water-glass forms a very compact mass. If a piece of chalk be plunged into a moderately concentrated solution of water-glass, and left for about two days in the solution, then taken out and dried, and again put into a somewhat more dilute solution, it becomes completely soaked with the fluid, acquires on drying a hardness even scarcely inferior to that of marble, and will take a good polish. Water does not soften it, though it removes a small quantity of alkali. The

chalk is also considerably increased in density. Powdered chalk or marble acts in the same manner upon water-glass, forming a compact mass, which may be used as cement. With magnesian limestone, water-glass forms a mass even harder than with pure carbonate of lime.

According to Fuchs, the alkaline silicate is not decomposed by the carbonate of lime, but unites with it directly, forming a compound analogous to the natural mineral, *cancrinite*, which is a compound of carbonate of lime with silicate of soda and alumina. Kuhlmann, on the other hand, regards the product of the action of water-glass on carbonate of lime as a *silico-carbonate* of lime, supposing that part of the carbonate of lime is decomposed by the alkaline silicate, forming silicate of lime, which then unites with the undecomposed portion of the carbonate.

Perhaps the most probable view of the matter is, that both these reactions take place at once, the one or the other playing the principal part, according to circumstances. When the process takes place at ordinary temperatures, and with free access of air, it is certain that the hardening of the stone is due in great part to the agglutinating action of the silica separated from the water-glass by the action of the carbonic acid of the air. Kuhlmann silicified two balls of chalk of the same size and the same degree of porosity, by immersion in a solution of water-glass, then exposed one of them to the free action of the air, and kept the other under a bell-jar, in an atmosphere deprived of carbonic acid. The former acquired a greater degree of hardness than the latter. The silicification may, however, be produced with still greater facility by heating the limestone with a soluble silicate under pressure. Porous limestones plunged into a bath of silicate of potash contained in a high-pressure boiler, exhibit, when taken out, all the characters of compact silicious limestone. In this case, the effect is evidently independent of atmospheric action, and can only be attributed to the formation of silicate of lime.

When the action takes place in the open air, the carbonate of potash separated from the water-glass, produces on the surface an almost invisible exudation, which, however, gradually diminishes, and at last disappears without affecting the surface of the stone. This exudation may be prevented by the addition of hydrofluosilicic acid, which likewise adds to the hardness of the stone. (Kuhlmann.)

On sulphate of lime, water-glass acts in the same manner as upon

carbonate; but the resulting mass is less compact, partly because the action is more rapid, partly because the sulphate of potash or soda formed by the decomposition crystallizes and disintegrates the surface of the stone. The silicious solution should therefore be more diluted, so as to render the action slower.

These reactions of the soluble silicates have been applied in various ways to the formation of artificial stone for building and ornamental purposes, and to the preservation of the stone of buildings actually constructed.

Artificial Stone.—Mr. Ransome, in 1844, patented a process for preparing artificial stone by mixing a solution of water-glass, prepared in the manner described at page 74, and concentrated to the density of 1·750, with sand, broken stone, or other silicious matter, and subjecting the mass to pressure in moulds by hydraulic or other mechanical power. It was then left to dry at common temperatures for about 24 hours, and afterwards placed in an oven heated to the temperature of boiling water, or even above that point.

The stone thus prepared was found to be excessively hard, close, and uniform in texture, and capable of being moulded into any desired form; but on exposure to a moist atmosphere, it gradually became soft, and was easily disintegrated. To remove this difficulty, it was necessary to subject the stone to a bright red heat in a kiln. The alkaline silicate was thus made to combine with an additional portion of silica, and form an insoluble silicate, which was not affected by moisture or other atmospheric influences. By varying the proportions and strength of the soluble silicate, it is possible in this manner to produce stone of any required degree of density and texture, from that of the most open and porous stone, suitable for filtering water or other liquids, to that of the hardest and closest grained stones, like granite. It was found, however, that when the stone thus prepared was practically used on a large scale, and in exposed situations, a salt effloresced on its surface, causing an unsightly appearance, and leading to apprehensions that disintegration would shortly follow. This salt was found to be sulphate of soda, derived partly from the soda-ash with which the solution of caustic soda had been prepared, partly from the lime used to render it caustic. This impurity was subsequently removed by treating the soda-lye with caustic baryta or a soluble baryta-salt, before introducing it into the boiler with the flints. By this means a water-glass was obtained free from

sulphate, and the troublesome efflorescence was got rid of. A patent for this improvement in the preparation was taken out by Mr. Ransome on the 3rd of July, 1853.

The stone prepared by this improved process is capable of receiving the finest and sharpest impressions, and possesses all the characteristic properties of the best natural sandstones. It is not liable to shrinkage or distortion under the operation of firing; it may be readily worked by the chisel, like other freestones; and by a series of experiments lately made at the testing-house in Woolwich Dockyard, its power of resistance to a steady transverse strain has been found to exceed that of various natural sandstones, in the proportion exhibited in the following table:—

Ransome's artificial sandstone	100
Darley Dale stone	81
Grimshill stone	37
Portland stone	33
Aubigny stone	31
Bath stone	13
Caen stone	12

Blocks of this artificial stone also, 2 inches cube, resisted a crushing weight of 21 tons, whilst similar blocks of Darley Dale crushed with 16½ tons. These figures are the mean results of three experiments upon each of the stones alluded to, and furnish satisfactory evidence of the suitability of the material for purposes of construction; and so far as experience has yet shown, it is in no way injuriously affected by the alternating influences of the atmosphere, even in the most exposed and unfavourable situations.

Mr. Ransome has also patented two other processes for the preparation of artificial stone with water-glass. The first of these (dated 23rd March, 1855, No. 645) consists merely in preparing the alkaline silicate in the dry way, instead of boiling the materials together under pressure, as in the process above described. A mixture of 5 cwt. of sand, 4 cwt. of soda-ash (containing about 50 per cent. of alkali), and ½ cwt. of charcoal, or 15 cwt. of sand, 10 cwt. of potash, and 1 cwt. of charcoal, is heated till it vitrifies; and the glass, after being broken up, is dissolved in water at the boiling heat or under pressure; the solution concentrated to sp. gr. about 1·170, is mixed with sand, clay, &c., and the mixture is treated as above; or the soluble glass, ground to fine powder, is mixed with the other substances, together with water.

The other process (patented 27th Sept., 1856) consists in adding

to the composition of artificial stone prepared with sand, clay, &c., and a soluble silicate, a substance which will fuse more readily than the sand, and will run into and fill the pores of the stone, thereby increasing its density. The substance used for this purpose is pumice-stone or a readily fusible glass.

(*a*) Finely powdered pumice-stone is mixed with a solution of water-glass (sp. gr. 1·700), and the pasty mixture is moulded into balls of about an inch diameter, which are fused in an ordinary crucible. The fused mass is ground to powder, and again mixed with the silica solution, so as again to form a paste; and in preparing the artificial stone, the ingredients are mixed in the following proportions by measure:—

Silicious sand	30 parts.
Finely powdered silica	10 parts.
Solution of silica, or what is called silicious cement (see Specification of Ransome's patent, 22nd Oct., 1844)	5 pts. of sp. gr. 1·700.
Powdered pipe clay	5 parts.
Pumice-stone prepared in the way above described	5 to 10 parts.

These materials are mixed together and treated in the way described in the specification above referred to.

(*b*) The pumice-stone in the mixture may be replaced by an equal quantity of an easily fusible glass, prepared by melting together in a reverberatory furnace or crucible, 100 parts of silicate of soda of sp. gr. 1·400 and 100 parts of oxide of lead.

Professor Way and Mr. J. M. Paine have patented a process (17th Nov., 1852, No. 771) for preparing artificial stone, bricks, tiles, and other kinds of burnt ware, by the use of certain beds or strata of earth rich in *soluble silica*, either alone or mixed with ordinary clay, and either with or without the addition of lime or other alkalies or alkaline earths. The peculiar strata of earth here spoken of are found at the base of the chalk hills in Surrey and elsewhere. To be economically available for the purpose, they should contain at least 10 per cent. of silica in that peculiar state in which it is dissolved by boiling with caustic alkalies in open vessels. The different kinds of burnt wares are produced by a proper adjustment of the quantity of soluble silica in relation to the composition of the clay with which it is mixed, and by a greater or less temperature and length of time in the burn-

ing. The details of the process are described in the specification as follows:—

"To produce a superior kind of plain or ornamental brick or tile or slab, suitable for the lining of walls, we proceed as follows: Having ascertained by chemical examination the proportion of soluble silica contained in different samples of the earth in question, we reduce such earths to powder by mechanical means, as is well understood. We find 15 to 30 per cent. of soluble silica to be the most suitable for the purposes mentioned when using the earth alone; or we mix the requisite quantity of the earth containing a higher per centage than those given above of soluble silica, with ordinary clay, in such relative quantities that the mixture shall contain the proportion of soluble silica above stated.

"Having prepared the materials by either of the above methods, we proceed to mould the bricks or other articles, either by pressure or in the ordinary way. When pressure is employed, we find it desirable to use the materials in a slightly damp state, but not so much so as is usual in the making of bricks from clay. In fact, we prefer to use the materials as dry as may be, having reference to the mode of moulding resorted to. The bricks, or other articles, being moulded, are to be dried in the air or in drying chambers, and are then to be burned in the usual way in suitable kilns. The degree of heat, however, and the length of time occupied in the burning, materially affect the character of the article produced. For instance, a gentle burning produces a material comparatively soft and capable of being sawn, cut, or planed like stone or wood; it is therefore sometimes desirable to stop the burning at this point, and to give to the articles, by the use of tools, a higher degree of finish and sharpness than is possible by the method of moulding before described. And the goods, when so worked up, may be a second time heated, and carried, by an increased temperature and duration of the firing, to a much greater degree of hardness and strength. And with a sufficiently elevated temperature, the material may be made of extreme hardness, so as to be capable of taking a high polish like granite. In this latter form, we propose to employ it in the manufacture of mantel-pieces, table-tops, and other articles requiring such degree of hardness.

"We have stated that, for the manufacture of moulded articles, we employ a mixture in which the proportion of soluble silica

varies from 15 to 30 per cent.; when it is intended that the material produced should be employed as stone, and be cut or tooled, it is desirable to employ a larger proportion of soluble silica, which is found to render the product more granular and open in texture. The same is the case when bricks are intended for the building of furnaces or kilns, and in other cases where they will be exposed to a high temperature; and we find that in making fire-bricks, the proportion of soluble silica may with advantage be as high as from 35 to 45 per cent.; but it is to be observed that, when present in above a certain proportion, the silica destroys the ductility of the mixture, which cannot then be moulded by hand as ordinary clay, but must be subjected to pressure.

"We have hitherto spoken only of the mixtures of the different earths containing soluble silica, with each other, or with ordinary clay. But we find that a different and for many purposes very valuable kind of material is obtained by mixing with these ingredients a certain proportion of lime or other alkali or alkaline earth; thus, to produce a yellowish white or lemon-coloured stone, in imitation of the best building-stones, we employ a mixture of earths as before described, in which the soluble silica is in the proportion of from 35 to 45 per cent. with 8 or 10 per cent. of lime. The mixture may be moulded by hand or pressed into moulds as before described (the latter being the preferable method), and afterwards dried and burned. We employ lime in the state either of burnt lime, slaked or unslaked, or in the state of carbonate of lime or chalk. We have found that the mixture, when made with slaked lime, gives the best results; but in some cases, chalk may be advantageously employed, as being the most economical.

"We have found that, by varying the proportions of soluble silica and of lime in relation to the clay, we are enabled to produce different kinds of stone, more or less resembling natural stone, fitted for building and other purposes, and this stone is capable of being cut with tools after being fired. We have also found, that the addition of a small proportion of lime to a mixture containing a high per centage of soluble silica, produces a good fire-brick."

Mr. Harris Hardinge, whose method of obtaining a solution of silica has been already described (p. 75), applies it to the pro-

duction of artificial stone, marble, &c., as follows (Specification, 29th May, 1844):

"To form stones for building, I take pebbles and angular pieces of broken stones, and mix the same up with the liquid quartz, and by mixing in various kinds of argilaceous loam and scoria from iron furnaces, different colours can be produced, the quartz forming the cement to make the particles adhere into a very strong and beautiful mass. The blocks of artificial stone may be formed in moulds, and afterwards ground off, or covered with a coating of liquid quartz, which forms a smooth polished surface.

"To form artificial marble, or composition for spreading on metallic or other surfaces to represent marble, I take the ordinary hydrate of lime, and introduce carbonic acid gas (which gas may be obtained from the charcoal burned in the furnace *d*, Fig. 15, p. 75), together with the liquid quartz, in the proper proportions so as to produce crystallization, which may be aided by electricity (?) if desired. The composition may be coloured by any known process with mineral oxides, so as to imitate any desired character of marble or precious stones, and by introducing kaolin a pure white marble is imitated. To make composition suitable for furniture, I take the ordinary composition or stucco used for picture frames and similar ornaments, and introduce into the same while being made, the liquid quartz and carbonate of lime or alumina, and colour the same to imitate rosewood or any desired article. This composition may be made into articles of furniture, or it may be placed on any article as a coating. A bright and durable varnish may be formed by mixing this liquid quartz with the gum resins, by the addition of mutual solvents, forming a hard and most durable varnish, and also with gelatinous substances, forming a composition or varnish which has the appearance of pearl. By mixing with the liquid quartz different mineral colours, and applying the same to glass, a durable and beautiful character of stained glass will be produced, and alone the liquid quartz will produce a semi-transparency of great beauty when applied to glass."

Mr. Joseph Ellis, of Toronto, in Canada, manufactures artificial stone of various kinds by cementing together pulverized stone, brick, earth, &c., by means of a soluble alkaline silicate mixed with cream of lime. Silicate of lime is thus produced, which is a

firm, compact, insoluble substance; and if, at the time of mixing the two liquids, other materials are added, to which either or both of the solutions have an affinity, the whole becomes consolidated into one mass of artificial stone; thus iron, zinc, copper, alumina, tin, or other metals, or oxides, carbonates, chlorides, oxychlorides, or metallic salts or compounds, may be introduced; or silica, baryta, strontia, or carbonate of lime or other earthy matters may be employed. To imitate various stones, the natural stone is ground to powder more or less fine, or partly into fine powder and partly coarse, and after being cleansed from impurities, is made into a thick paste with the two solutions of silicate of potash and lime, then put into a smooth metallic or other mould of the form required, and subjected to pressure. The mould may be oiled or greased to prevent adhesion. A solid block of the required form of artificial stone is thus obtained, and may be removed from the mould and dried. Artificial marble with ornamental mouldings may thus be manufactured from refuse or fragments of marble or from shells; granite, porphyry, malachite, and other stones may be imitated in a similar manner. By mixing different-coloured stones in the same paste, or by mixing the different pastes together, or adding colouring matters thereto, various veined or variegated stones may be manufactured.

The aforesaid solutions are also used to combine or consolidate clay or marl or brick earth, either raw or burned, or baked coal, wood, kelp, peat, bones, ashes, or slag from iron works or metallurgic operations, with carbonate of lime or lime, or both, and with or without the addition of sand or sandstone. Ground or powdered marble or other stone mixed with a small quantity of hydraulic or other lime and slightly damped, is consolidated by pressing it into moulds in the same manner. Sand or sandstone, however, is not to be used alone with lime, as it requires the addition of some other stone, earth, oxide, or alkali, to produce the required combination and consolidation. The artificial stone is not always made of the same materials throughout; thus, a mould may be partly filled with a fine or valuable material or paste to form the exterior surface, and the other parts of the mould with a coarse or cheaper material. Plates of zinc or tin are used when required for keeping the materials separate while filling the moulds, and then withdrawn, or the two materials are filled in simultaneously through a divided hopper. The water employed may be pure and clean; or tan-pit water, dye

water, bog-water, or water charged with lime or iron, or other mineral or metal capable of combining or consolidating with lime or other liquids having an affinity for lime, such as blood and petroleum, may be added to or substituted for the water. For some purposes, the blocks of artificial stone are subjected to a high temperature or red heat, so as to vitrify or partly vitrify the composition. In most cases, it is preferable to subject the composition to great pressure while in the moulds; this pressure may amount to one or more tons on the square inch. For many purposes, however, a less pressure will suffice, and in some cases the pressure obtained by moulding the materials in the way in which bricks are moulded is sufficient. Instead of making the composition into blocks, it may sometimes be employed directly in lieu of concrete for making foundations, and in lieu of plaster or cement for covering or cementing walls, and for various purposes of a like nature.

In some cases, the composition or the blocks made of it are saturated with linseed oil, or wax, or varnish, or fatty, or oily, or tarry substances, to render them impervious to damp; or they are exposed to damp, or steam, or hot water, after taking them from the moulds, to assist in effecting the combination of the materials.

The cementing power of the soluble silicates has also been applied by Mr. Ransome for combining small coal into blocks for artificial fuel, and for cementing and preserving wood. The processes are thus described in the specification of the patent (dated 10th May, 1845, No. 10,665):

"In cementing small coal, I usually take about one hundred parts of coal dust or small coal, and mix it intimately with from one-tenth to one-twentieth of its weight of the silicious cement prepared as before described (page 74); but it is obvious that the quantity of cement required will vary according to the size of the particles of coal used in the mixture, the design being in all cases to economize as much as possible the use of the cement, and yet to produce the fuel of the required stability when dried. The mixture thus prepared is put into suitable moulds to form lumps or blocks, and subjected to hydraulic or other mechanical pressure, after which it is taken from the moulds and allowed to dry at the common atmospheric temperature for a few hours, when it may be removed and placed in an oven or hot room.

I also find it advisable, for the purpose of effecting the more perfect combustion of artificial fuels generally, as well as my own above described, to form one or more holes through each lump or block of fuel for the free admission of air during the process of combustion; and this is easily accomplished by inserting in the moulds one or more plugs or cores slightly tapering, which can readily be withdrawn after the fuel is compressed.

"In cementing timber, I propose to saturate or impregnate it with a solution of silica in such manner as to cement the fibrous part of the wood with the silica, so as to form a solid and durable mass. And for this purpose I proceed as follows: I place the wood in an air-tight vessel of suitable form to receive it, and having abstracted as much of the air as may be practicable by an air-pump or other convenient means, I admit a sufficient quantity of the silicious cement, before described, to cover the wood entirely; and for the purpose of causing the cement to penetrate further into the pores of the wood than would be effected naturally, I apply artificial pressure by means of a pump. The wood is afterwards removed and immersed in some acidulated or saline solution, such, for instance, as a solution of muriatic or hydrochloric acid, or any other solution which will render the silica insoluble."

Hardening and Preserving of Building Stones.—The stones generally used for building are limestones, oolitic or otherwise, magnesian limestones, and sandstones. These are all freestones, composed for the most part of grains, whether of quartz, carbonate of lime, or carbonate of magnesia, and generally cemented together with carbonate of lime. They vary considerably in hardness and density, those of densest character being generally the least absorbent and most durable. Now, when these stones are exposed in the damp impure atmosphere of large manufacturing or populous towns, they are soon acted upon by the carbonic or sulphuric acid contained in the atmosphere and held in solution by the rain-water, which is readily absorbed within the natural crevices or between the grains of the stone. Moreover, this water contracts and expands with variations of tempeture, and tends further to disintegrate the stone, especially in frosty weather. By the action of these causes, a process of decay is set up which continues till the entire surface of the stone is destroyed, and the building seriously disfigured. Attempts have

been made at various times to remedy these evils by the use of varnishes made of oily or fatty matters; but these, besides producing an unsightly appearance, are liable to rapid decomposition from the oxidizing effects of the atmosphere.

Much better results are obtained by the use of the soluble silicates, either alone or in combination with lime; such mixtures have indeed been used with the best effect both in this country and on the continent.

M. Kuhlmann uses for this purpose a solution of silicate of potash. Silicate of soda, though it produces the same effect in hardening the stones, is said to give rise after a while to unsightly efflorescences. The liquid used by M. Kuhlmann for covering buildings is prepared by mixing a solution of potash water-glass of 35° Beaumé, containing a third of its weight of solid silicates, with twice its volume of water; or by dissolving the solid silicate of potash in six times its weight of water. The solid silicate dissolves more readily in water already slightly charged with silicate than in pure water. This weak solution is heated to ebullition in an iron boiler, and the solid silicate added in powder or in small pieces. The proportions just mentioned need not however be rigorously adhered to. It must be observed, however, that too weak solutions require frequent repetition of the process of impregnation, whilst too concentrated solutions are ill suited for thorough penetration and, consequently, for thorough hardening of the stone.

The mode of applying the silicious solution varies according to the nature of the building to be treated. In more recent structures it may be applied at once; but in older buildings the stones require to be cleansed in order to facilitate absorption. Mere washing rarely suffices; scraping will always be found preferable whenever it is practicable; or else washing and scrubbing with a hard brush, or with a solution of caustic potash; acidulated water must not on any account be used.

If the stone is of small size, such as a statuette or piece of ornament, the silicious solution is applied by simple immersion for some hours, the process being repeated several times. Large surfaces are coated with the silicate by means of fire-engines or large syringes with broad rose nozzles, care being taken to place at the foot of the walls gutters made of burnt clay, plaster, or cement to collect the excess of liquid, which may serve for fresh operations. When the silicification is applied to certain portions

only of a building, *e. g.*, upon sculptures, a soft brush may be applied. In all cases, the window panes must be covered with cloths to protect them from being sprinkled with the silicious solution, which would leave spots irremovable when dry.

Between two successive applications of the silicious solution, an interval of several hours, or, better still, of a day, should be suffered to elapse. Three applications, on three consecutive days, will generally be found sufficient. If the operations be repeated too often, the stone will be found coated with a vitreous layer, of shining, disagreeable aspect, necessitating repeated washings with water after the last sprinkling. There are, however, stones so porous that this inconvenience will scarcely show itself.

The application of the silicate may be effected all the year round, except during hard frost. Dull weather is preferable to warm and dry weather. When the sun is shining warm, it is advisable to pretect the work by means of cloths to prevent too rapid desiccation.*

In the report of the French Government Commission charged with the examination of Kuhlmann's process of silicification, it is stated that the treatment just described has been applied at the Louvre and the Cathedral of Notre Dame, in Paris, and to several buildings, both public and private, in other towns of France, and has yielded satisfactory results.

On the other hand, it appears from the observations of Mr. Ransome, that the application of the simple silicate of potash or soda as a preservative of stone buildings is attended with very uncertain results, at least in the climate of England; one great cause of failure arising from the fact, that the silicate, being applied in the soluble form, is liable to be removed from the surface by rain, or even by the ordinary humidity of the atmosphere, before the alkali can absorb sufficient carbonic acid to precipitate the silica in an insoluble form. But another great and serious defect of the process is that the silica, even when thus precipitated, is simply in the form of a gelatinous hydrate, possessing very little cohesion, and, therefore, capable of affording but little (if any) protection to the stone.

All these inconveniences are obviated by using, in addition to

* A patent for carrying out this process in England was secured in 1853 (13th April, No. 367), in the name of P. A. Moreau, Patent agent. The name of the inventor is not given in the specification; but the process is evidently that of M. Kuhlmann.

the soluble silicate, a solution of *chloride of calcium*, whereby there is produced, independently of the action of the air, an insoluble precipitate of *silicate of lime*, possessing strong cohesive properties, and perfectly indestructible by atmospheric influences. Silicate of lime is indeed one of the strongest cementing media with which we are acquainted. It is the substance which imparts the valuable properties to our best and strongest hydraulic cements, insures the stability of solid concrete masses, and has conferred such enduring properties on the old Roman mortars.

This process was patented by Mr. Ransome for both England and France in the year 1856. The mode of application is as follows: The stone, or other material of the building, is first cleaned to remove any extraneous matter from the surface, and then brushed over with a solution of silicate of soda or potash, the strength of which may be varied according to the nature of of the stone; and this when dry is followed by a solution of chloride of calcium, applied also with a brush. The lime immediately combines with the silica, forming silicate of lime, within the pores of the stone; and the chloride of sodium formed at the same time is removed by washing with water.

The first practical application made of this process was upon two of the buttresses of the river front of the new Houses of Parliament, the stone of which was at the time in a state of rapid decomposition. It has been eminently successful. Speaking of the result, Mr. Ransome writes, in the Journal of the Society of Arts (Nov. 4, 1859), "Although nearly three years have elapsed since these portions were so treated, no indications of decay have since appeared; but, on the contrary, a small excess of silicate of lime, which was inadvertently left on the surface of the stone through the carelessness or inexperience of the workman, is still present, and cannot even now be removed by any mechanical means, without at the same time destroying the face of the stone.

"During the past three years, the efficiency of this process has been tested under every variety of circumstances that has been suggested, with the most satisfactory results. Masses of soft and easily decomposible stones have been treated over only portions of their surfaces, and afterwards exposed to the alternating influence of heat and cold, and of wet and dry atmospheres. In no instance has decay since been visible upon any portions of the stones which have been properly treated; whilst in almost every

instance, the portions of the same stones not treated have manifested more or less decay; and pieces of the same stone have been taken, some of which were treated by the process, and an equal number were left in their natural state; each was carefully dried and weighed, and then all were immersed together in a dilute solution of sulphuric acid for an equal length of time. Upon being removed from the acidulated solution, it was found that in every instance, the stones which had not been treated by the preservative solutions were entirely broken up—falling into fragments; but that, without exception, every stone that had been so treated was entirely unacted upon, had retained all its sharpness of outline, and had not diminished a grain in weight.

"The process herein described is equally applicable to bricks, cement, plaster, and even to common chalk. It renders these materials equally capable of resisting the varying and destructive influences of any climate, prevents all liability to dampness or vegetation, as also the absorption of smoke or dirt, which produces discoloration, so frequently disfiguring our finest edifices.

"Many instances may be adduced as practical evidence in support of the foregoing remarks; but I need only further mention that, amongst other important buildings, the process has been applied upon the Baptist Chapel, in Bloomsbury Street, London, upon the Royal Pavilion at Brighton, the Custom-house at Greenock, and is now being used upon Craigsend-house, near Paisley, and upon Lennox Castle, near Glasgow." *

The use of silicate of lime as a paste or cement for preserving buildings is also included in Mr. Ellis's patent, noticed at page 86, the date of which is, however, subsequent to that of Mr. Ransome's. Moreover, the silicate of lime produced by Mr. Ellis's method, viz., by mixing silicate of potash or soda with cream of lime, would not be likely to penetrate into the interior of the stone, so well as when produced by first washing the stone with the alkaline silicate, and afterwards with solution of chloride of calcium.

* See the report of a lecture "On Building Stones,—the Causes of their Decay, and the Means of Preventing it:" delivered before the Society of Arts, March 2nd, 1860, by G. R. Burnell, Esq., C. E. In the discussion which followed, strong testimony as to the efficiency of Mr. Ransome's process was given by Professor Ansted, Mr. Robert Hunt, and other gentlemen well acquainted with the subject. (Journal of the Society of Arts, viii. 240).* See also an article on the same subject by Professor Ansted, in Macmillan's Magazine, April, 1860.

2. SILICIOUS PAINTING—STEREOCHROMY.

This important application of water-glass is based upon its property of causing colours to adhere well, and of imparting to pictures as well as to coats of paint, great durability and power of resisting destructive influences. This kind of painting is called *stereochromy* (from στερεὸς, solid, and χρῶμα, colour) by Fuchs, to whom we are indebted for the first experiments on the subject. It is applicable to mural painting, for which it possesses many advantages over ordinary fresco painting, both in facility of execution and in permanence; also to painting on plates or vessels of earthenware, lithographic stones, plates of clay-slate, &c.

Two methods of silicious painting have been proposed, viz., that of Fuchs, in which the colours, ground up with water, are laid upon a prepared surface and afterwards fixed with a silicious solution, and that of Kuhlmann, in which the colours are ground up with the alkaline silicate.

Fuchs's Method.—To produce a good stereochromic painting, it is in the first place necessary to look to the *foundation* of the picture, which consists of a *lower* and an *upper* layer of mortar-cement. This groundwork must have a thorough and stone-like solidity, and a perfect adhesion to the wall, and must be capable of absorbing the water-glass in all its parts with equal avidity. The first layer or substratum is formed of ordinary lime-mortar; its object is to equalize the unevenness of the wall, and to cover the stone completely. The sand should be of even grain, neither too coarse nor too fine; it may be either calcareous or quartz-sand, but in either case must be well washed before use. The lime must be properly slaked and sparingly employed, so as to render the cement, which must be made up with distilled or rain water, rather poor than otherwise. A rich cement would not absorb the water-glass readily, and might cause it to crack.

The plaster covering thus prepared must be well dried, and exposed to the air for several days, that it may absorb carbonic acid, and be converted into basic carbonate of lime; for if the lime were to remain caustic, the water-glass would be immediately decomposed by it, and would not penetrate to the wall—a matter of necessity if a good cementation is to be effected. The saturation of the lime with carbonic acid may be accelerated by moistening the wall several times with a solution of carbonate

of ammonia. When it is dry, and the ammonia has evaporated, it is washed several times with water-glass, allowing it to dry each time, and continuing the application till complete saturation is attained. The silicious solution used must be either soda or double water-glass (p. 73), either of which is absorbed more easily than potash glass: it should be moderately dilute. To ensure uniformity of composition in the substratum, it will be necessary to give the thicker portions of it an extra treatment with the silicious solution.

The lower ground being thus prepared, the upper layer may be added soon after. Great attention must be paid to the preparation of this layer, as the success of the painting is in a great measure dependent upon it. It is about $\frac{1}{10}$ of an inch thick, and consists, like the lower layer, of lime-mortar, which should be made with distilled or rain water, and well washed sand (either calcareous or quartz-sand), of a grain not exceeding a certain size, and with just a sufficient quantity of lime to prevent cracks and ensure complete absorption. To obtain the right grain, it is best to pass the sand through a sieve. Very fine powder must be rejected, because it renders the mass too compact and less absorbent. A rough ground, such as is produced by coarse-grained sand, is rather advantageous in painting. Kaulbach, the celebrated painter of Munich, who has had much experience in this kind of painting, says it ought to feel like a rasp. A difference must, however, be made, according as the picture is to be viewed at a long or a short distance, a coarser ground being required in the former case than in the latter.

When the coat of mortar has become dry, it is sometimes rubbed over with a sharp sandstone or iron straight-edge, to remove the layer of carbonate of lime which has formed during the drying: it is better, however, to remove this coating by means of dilute phosphoric acid. The phosphate of lime thereby produced binds well with the water-glass; whereas, if friction is resorted to, there is a risk of detaching small pieces, and leaving cavities, which have to be filled in again.

When the ground thus prepared is well dried, it is impregnated with water-glass, using for the purpose the double water-glass (silicate of potash and soda) clarified with liquor silicum (p. 73), and diluted with an equal bulk of water. It is sufficient to repeat the application twice, allowing time for the first washing to dry. Too much water-glass closes up the pores, and prevents the ground

from taking the colour. If too much has been used, either the whole layer of plaster must be removed, or the painter must wait till the further contraction of the water-glass renders the ground sufficiently porous; the change may be accelerated by applying heat, which is best done by burning alcohol upon it. The ground having been thus prepared, the painting may be at once proceeded with; but there is no necessity, as in fresco painting, for going to work immediately; on the contrary, delay increases the capacity of absorption which the ground already possesses.

The colours are ground with pure water, and used by the artist on the prepared surface, care being taken to moisten the wall frequently with water, in order to displace the air from the pores, and ensure the adherence of the colour. This syringing with water must be done with moderation, and only as often as is necessary. Great care must be taken not to wet too much those parts which have been painted over, because the freshness of the colours is thereby impaired; it appears that the water washes the finest and least powerful particles of the colour up to the surface. This inconvenience is greatest in places which have to be painted over repeatedly and moistened each time. A remedy has, however, been found in brushing away these fine particles of colour after they have dried, and before the picture is fixed, with a very fine brush, by which means the picture is restored to its original freshness.

Nothing now remains to be done but to fix the colours properly, to which end the fixing water-glass (p. 74) is more especially adapted: it should be diluted with half its bulk of water.

The colours which adhere but slightly do not allow of the brush being used; and it is necessary to sprinkle the painting with water-glass, in the form of a fine shower or mist, very carefully at first, so as not to displace the colours or cause them to run one into the other. A syringe for the purpose has been invented by Professor Schlotthauer. The operation of alternate sprinkling and drying is continued till the colours adhere so firmly that they cannot be rubbed off with the finger. Some colours appear to be more difficult to fix than others. This is especially the case with the so-called meagre colours, like black. These require more water-glass, which is added by means of a fine brush. The adhesion of the colours appears, however, to be best ensured by careful mixing.

The preceding is a general outline of the method by which

Kaulbach and Echter have executed four large stereochromic paintings in the new museum at Berlin, which are generally acknowledged to exhibit a great advance in the art of monumental painting.

The success of stereochromic painting appears to depend mainly on the careful preparation of the upper layer of plaster or painting ground; errors are easily committed in this part of the process, and have frequently been a source of failure. For this reason, Professor Fuchs endeavoured to obtain a surer method of preparing the painting ground, and in his latest essay on the subject, he recommends the preparation of this upper coating with water-glass cement—*i. e.*, mortar in which the lime is replaced by water-glass. The sand to be mixed with it may be either pounded marble or dolomite, or quartz-sand mixed with a little dry slaked lime. The mixture must be very intimately made, the water-glass being used in quantity sufficient to give the mass the consistency of ordinary mortar.

This cement is laid on equally thick over the first plaster coat, properly smoothed, and allowed to dry. It possesses many advantages over the lime-water subsequently impregnated with water-glass. Its preparation is simple, and the water-glass being equally diffused throughout the mass, and in immediate contact with the lime coating, ensures uniform cementation and silicification, as well as perfect adhesion to the wall. Moreover, during the repeated moistening of the picture, no lime will be drawn to the surface to disturb the colours, because no soluble lime is left in the mass; neither can any incrustation of carbonate of lime be formed, requiring rubbing with a stone to remove it.

The cement, when dry, is as hard as stone. At first it has but little absorptive power, because its pores are filled with water-glass. After a few days' exposure to the air, it becomes more absorptive, in consequence of the contraction of the silicious compound, but at the same time it loses considerably in solidity, so that it requires to be saturated once or twice more with water-glass, care being taken, however, not to stop up the pores by using too much. The burning of spirits of wine on the surface might, perhaps, ensure the required degree of porosity. If carbonate of soda effloresces on the surface, it is a sign that the plaster has set well. The efflorescence is easily removed with a wet sponge, and the ground will then be found harder than

before. The painting may then be proceeded with in the manner already described.

Stereochromic paintings may be executed on old walls already covered with plaster, provided the plaster is sound and in good condition, thoroughly dry and free from efflorescent salts, and adhering firmly to the wall. It should be rubbed with a rough sandstone, and well smoothed; and if it is then found to possess the requisite degree of absorptive power, it may be impregnated with water-glass and used for painting as above.

Other substitutes may also be used. Plates and vessels of earthenware, if only moderately burned, form a very good ground, after being saturated with water-glass and covered with a layer of the water-glass cement just described. Easel pieces of considerable size may be painted on earthenware plates, the only limit to their size being the difficulty of managing plates of great weight. The plates should not be thicker than three-quarters of an inch, and with a flat but not smooth surface. They should not be too much burnt, or they will not absorb well. Frequent saturation with double water-glass diluted with half its volume of water, imparts to them a solidity such as strong burning could not do. Should they lose their absorbing power by the addition of too much water-glass, they have only to be warmed for some time, *e. g.*, by burning spirits of wine upon them. If it is required to paint immediately on such a ground, a little fixing water-glass should be added to the colours, especially to the meagre ones. Objects made of burnt clay, such as figures, ornaments, vases, and goblets, may likewise be painted in this manner, due attention being paid to the quality of the ware. The same process may be applied to earthenware stoves, the tiles being first repeatedly saturated with water-glass and heated. Cast-iron stoves may also be painted stereochromically. The colour must be laid on while the iron is warm to the touch, otherwise it will fall off when the stove is heated.

Plates of *lithographic stone* may be used as a ground for stereochromic pictures: the first trials were indeed made with such stones. They require to be coated with a thin layer of water-glass cement, mixed with somewhat coarse sand, to ensure the adhesion of the painting ground. When the cement is quite dry, the upper coat is put on, and the painting may be proceeded with. If the lithographic stone is treated with phosphoric acid, it takes

the colours well, provided they are mixed with water-glass; it is therefore probable that stones so treated might be used for silicious painting without further preparation. Plates of clay-slate, porous sandstone, and porous limestone, might also be used after due preparation.

The colours best adapted for stereochromic painting are the following:—

1 Munich white.
2 Munich black.
3 Munich brown.
4 Chrome green.
5 Cobalt green, light and dark.
6 Chrome red.
7 Oxide of iron, bright red, reddish brown, and violet brown.
8 Cadmium yellow, light and dark.
9 Chrome yellow.
10 Ultramarine.
11 Dark ochre; the same burnt.
12 Flesh ochre.
13 Gold ochre; the same burnt.
14 Terra de Siena.
15 Umber; the same burnt.

No organic colours, such as lakes, are admissible, because they will, sooner or later, be found to fade. Vermillion must also be rejected, because when exposed to light it darkens and ultimately turns black.

The colours ought to be ground as finely as possible, because they are thereby rendered more manageable and more adhesive. Chrome red alone forms an exception, because long-continued grinding turns it yellow. Cobalt blue shows a brighter blue after fixing, and light ochre becomes darker; these two colours cannot therefore be recommended for stereochromic painting.

The fixing process produces slight changes in all the colours of the painting, imparting to them a somewhat darker or more sombre hue, but this effect disappears after a while.

The colours ought to be as pure as possible, and especially free from anything that can decompose the water-glass, or cause it to coagulate, such as gypsum or sulphuric acid, which are frequently met with in red oxide of iron (colcothar caput mortuum) and in yellow ochre.

Stereochromic painting possesses decided advantages over ordinary fresco-painting. In the first place it is much more durable. Pictures painted in this manner have been exposed to the roughest treatment, and to the destructive action of smoke, acid vapours, quick changes of temperature, rain, hail, and severe frost, and

have come out quite uninjured. Six such pictures, painted on the outside walls of a country house on the shores of the Lake of Starnberg, have now been exposed to the weather for six years, and are still as fresh as if they had just come from the hand of the artist. Secondly, stereochromic painting is quite in the power of the artist, whereas fresco painting makes him a slave to the material. While engaged in the former, he can interrupt his work when he pleases, and can retouch his painting before fixing. as often as he thinks desirable. Stereochromy also possesses, in common with fresco painting, the advantage that the colours are not shining, and may therefore be viewed with equal facility in all directions.

Kuhlmann's method.—The essential difference between this method of silicious painting and that of Fuchs' is that the colours are ground up with the silicious solution, and consequently do not require so much preparation of the painting ground, or so much care in fixing. The mode of applying them varies with the nature of the ground.

In painting upon stone, upon a wall, or upon glass, &c., the colours, after having been ground with water and kept in a pasty state, are immediately mixed with a silicious solution of 15° to 20° Beaumé, and applied exactly as in oil or distemper painting, except when a very porous stone is used, in which case it is best to silicify the stone before applying the colours, to prevent too rapid desiccation. For glass and earthenware, the silicious solution ought to be more concentrated. Painting upon wood is equally efficient, provided the wood is not impregnated with resin, which repels the colour, as would be the case if silicious painting were applied over old oil-paint.

For the painting of rooms, a mixed style may be adopted, the painting being done in the usual manner in distemper, and the colours afterwards fixed with two layers of silicate of potash or soda, applied with a painting brush, the first layer with a solution of 6° Bm., and the second of about 10°, an interval of some hours being suffered to elapse between the two applications.

M. Kuhlmann has patented these and other applications of his silicious colours in England, in the name of A. E. L. Bellford, patent agent (4th July, 1855, No. 320). The processes are described in the specification as follows:—

"The solutions of alkaline silicate, which form the base of the

new or improved paints, are reduced to the proper liquid consistency for being used with the brush by mixing them with the greater part of mineral colours or pigments, either natural or artificial, that are at present in use, excepting of course those which are altered by the presence of the alkali, as Prussian blue, for instance. Some colours of the same kind are difficult to apply, and require great precautions, being rather strongly attacked by the solution of silicate of potash and by partially combining with silica, for instance, white lead, chromate of lead, &c. This latter class of colours must, therefore, be used with weaker solutions, or else in conjunction with substances having a weaker affinity for silica. It may also be observed that even the more insoluble kind of colours are attacked a little by the silicate; amongst these are the artificial or natural sulphate of baryta, which forms an exceedingly white and cheap base, and agrees very well with the silicate by thoroughly uniting with the same. Although this white base does not cover quite so well as white lead, yet it is preferable, on account of the low price at which it can be obtained.

"When the improved paints are used, the surface or object to which the paint is applied must sometimes be filled up or cemented, the same as when oil, turpentine, gelatine, starch, &c. is used. For this purpose, a cement or mastich is formed with the same solution, which is concentrated for the purpose, and compounded with fast-drying substances, such as white lead, artificial carbonate of baryta, phosphate of lime, chalk, ochre, oxide of manganese, of iron, &c., the mixture being applied to the joints. When it is desired to apply a considerable thickness of mixture, such as for mouldings, a petrifying cement is used, containing silicate as obtained in the dry process, as already described (p. 74), and mixed with quicklime and oxide of manganese, or of iron, and sand, all these substances being reduced to fine powder, screened and thoroughly intermixed, before being brought into the liquid state. The same petrifying cement is also used for rendering different kinds of lime hydraulic, or for making any mouldings or plastic works, repairs, or restorations, as with natural cement.

"The silicate colours above described may be rubbed over or smoothed down with pumice-stone; they can also be laid on in several layers and covered with a varnish made with a dilute solution of the same silicate that has been used for making the paint itself. The silicious paints may be applied, not only to stone and

wood, but also to metals, glass, and porcelain, these colours adhering very satisfactorily to metallic surfaces, ochre, and still better to oxide of manganese or of iron; and silicate may be used to preserve the iron from rust instead of minium (red lead) and linseed oil; also, by applying successive layers of a mixture of silicate and artificial or natural sulphate of baryta upon brightened surfaces of cast iron, a very durable and hard kind of enamel is obtained, which can be vitrified by heat, if required. Oxide of manganese may be used in the same way, and gives a black enamel of a similar description.

"The silicate colours produce remarkably fine results when applied to glass painting, and the pigments chiefly used for that purpose are transparent or opaque enamels ground fine. All the other colours, and also organic lakes, are equally applicable; but these latter are liable to get changed by the presence of free alkali, and are less durable than mineral colours. An imitation of dull ground glass is also formed by applying artificial or natural sulphate of baryta and the soluble silicates on glass, either cold, or vitrifying the same by heat, so as to produce a white enamel.

"For producing plain or flat tints on glass, the glass is lined by applying to its surface very thin sheets of coloured glass, which is done, after the pane has been covered with concentrated alkaline silicate, by sliding the coloured sheet or leaf to and fro upon the white glass, so as to expel the air and superfluous liquid from between the two, and thus obtaining double glasses which are perfectly transparent. In the same way plates or pieces of glass of any thickness and colour required, may be formed by fixing successive sheets of plate glass or of polished crystal upon each other. The pieces of crystal thus obtained will be found particularly useful in making lenses, and constructing optical instruments of any dimensions. For producing imitations of stained windows, the pieces or panes of glass which are painted upon or vitrified are joined by securing or glueing them together at the edges with concentrated alkaline silicate, which may either be pure or mixed with mineral matters to render the silicate insoluble; this gives to the edge-joint the appearance of an opaque line, which is rather narrow, and may easily be kept of the same width throughout, thus replacing the leads now used for that purpose. This mode of forming a joint is also applicable to incrustations or mosaic work in stone, wood, metal, &c.

"The processes above described for glass painting are equally applicable to porcelain, which may be ornamented with the most varied and elegant colours, either when it is enamelled or not (biscotto), the painting in the latter case being coated over with silicated varnish or enamel.

"In any of the applications above set forth, the varnish or enamel after some time becomes insoluble in water, even if it be boiling; this insolubility may still further be ensured by the addition of the colouring oxides, or of a small quantity of artificial carbonate of baryta, which dissolves in it at a gentle heat. In some cases, when the colours are not very siccative, they may be rendered more insoluble by washing the painting after it has hardened, with a dilute solution of hydro-fluosilicic acid, which fixes the potash; however, this means need but very seldom be resorted to. The paintings may be made still more insoluble by washing them with a weakened solution of muriate of ammonia.

"The new black colours or pigments, which are made with lamp-black, are as homogeneous, or mix as well as the others. In these colours, there is no danger of a double silicate forming; it will also be found useful to increase the drying powers of the silicate by adding a little artificial carbonate of baryta. The same precautions may be taken with respect to other colours which are not very liable to be attacked by the alkaline silicate. These black colours may also be used as printer's ink, giving a very fine and durable letter-press. As the silicated ink, however, is liable to get thick soon under the roller, a little treacle may be mixed with it to facilitate the work. Instead of black colours, any others may equally be applied to paper also by printing a colourless and concentrated silicious solution on the paper. The same is prepared for gilding and silvering; or the silicious solution may be used for fixing on paper and other surfaces thin leaves of metals, which are previously rendered adhesive merely by slightly damping them with saliva, or some gummy liquid. The silicious solution is further used for applying on paper, wool, or cotton powder, so as to produce an imitation of velvet; and also glass and emery powder, for producing sand and emery paper. The wool and cotton powder may also be applied directly to the walls. The processes described with regard to letter-press printing are also applicable to the manufacture of papers for hanging rooms, &c.

"The same means and processes may also be applied to fixing on fabrics certain adjective colours, such as ultramarine; and for printing on fabrics any lake-colours of organic origin, which give tolerably solid designs. By means of this silicious solution, linen or cotton cloth may also be coated with wool-dust on one or both sides, so as to imitate woollen stuffs. The colours may be fixed by using in suitable proportions any of the above substances employed for rendering the silicated painting insoluble, or any salt which decomposes the silicate that is still soluble will answer the same purpose.

"The silicious solution is employed as the base of a most unalterable writing ink. For this purpose, a brownish black liquid is prepared by boiling pieces of old leather with a solution of caustic soda or potash, and this alkaline solution is then saturated with silica in a state of jelly; if a deeper black is to be given to the ink, the carbonaceous ingredients of Indian ink must be added. The silicates of potash or of soda are also applicable for giving to fabrics a finish, which may be graduated at will, and renders them very water-tight.

"Another application of the solution of silicate is for mixing the same with paper and pasteboard pulp, for the purpose of rendering the paper and pasteboard made with it more substantial."

CHLORATE OF POTASH.

This salt forms transparent colourless crystals, of tabular form, belonging to the oblique prismatic system, and becoming under certain conditions, as by slower crystallization, longer and more apparently prismatic. It is inodorous, and has a cooling saline taste, resembling that of nitrate of potash.

It fuses at a moderate heat without decomposition, and, at a higher temperature (356° F. and upwards), rapidly evolves oxygen gas, with considerable intumescence of the mass and formation of chloride of potassium, KCl, and perchlorate of potash, $KO . ClO^7$. At a red heat, however, or at a lower temperature, if an addition be made of a metallic oxide, such as binoxide of manganese or black oxide of copper, the evolution of oxygen is

complete, no perchlorate is formed, and the residue consists wholly of chloride of potassium. In this case, the metallic oxide is not itself affected, but acts in an unexplained manner, or "catalytically."

Chlorate of potash is decomposed by oil of vitriol into bisulphate of potash, perchlorate of potash, and oxide of chlorine, with flame, and any combustible substances added to the chlorate are, in consequence, inflamed at the expense of the evolved oxide of chlorine.

When heated with combustible bodies, such as carbon, sulphur, or phosphorus, chlorate of potash detonates violently, moderate pressure, friction, or other causes, which induce a slight rise in temperature, being sufficient to produce the explosion.

This salt may be formed by various processes:—1. When chlorine gas is passed to saturation into a watery solution of caustic potash, and the liquid is kept for some time at the boiling point to decompose hypochlorite of potash, the resulting solution contains only chloride of potassium and chlorate of potash. The solution becomes saturated, and the chlorate falls out as a crystalline powder as it is formed, and is purified by draining, washing, and recrystallization.

The success of this experiment depends mainly upon the strength of the solution; for when this is formed by dissolving 1 part of caustic potash in 3 parts of water, the resulting liquid contains 1 equivalent of chlorate to 5 of chloride; whereas the product obtained by the use of a solution either stronger or weaker appears to contain fully 3 times as many equivalents of chloride to 1 of chlorate.

In this operation, the liquid is often tinged red by hypermanganate of potash, formed from the particles of manganese carried over mechanically from the vessel in which the chlorine is generated.

A similar result is obtained by substituting carbonate of potash for caustic potash, and, in either case, the chlorate and chloride are separated by virtue of their different solubilities, the latter salt always remaining in the mother-liquors.

A patent was granted in 1821 at Vienna to St. Romer, for the use of carbonate of potash in the solid form, the crystals being laid upon shelves or trays in chambers into which chlorine gas was introduced, just as in the manufacture of bleaching powder.

2. If a mixture of equivalent quantities of carbonate of potash and caustic lime be employed, rapid absorption takes place, all the lime remains as carbonate of lime, and the solution contains chloride of potassium and chlorate of potash.

3. An improvement upon the above processes consists in the direct use of bleaching powder, the so-called "chloride of lime," a substance now manufactured upon a vast economical scale. The powder is made into a "cream" with water, and submitted to continuous boiling or evaporation to dryness, whereby it is resolved into a mixture of chlorate of lime and chloride of calcium, a change the completion of which is indicated by the loss of bleaching properties in the mass. The residue, after evaporation, is treated with water, and chloride of potassium or sulphate of potash is added, whereby the chlorate of lime is decomposed, with production of chlorate of potash and chloride of calcium or sulphate of lime. The chlorate, amounting to about $\frac{1}{10}$ of the weight of chloride of lime employed, is separated from sulphate of lime by the insolubility of the latter, or from chloride of calcium by crystallization.

4. The process now generally employed consists in a modification of the last, in which the chloride of lime is formed in the same operation as the chlorate itself, instead of starting from a previously manufactured bleaching powder. Excess of chlorine is passed into a mixture of 300 parts caustic lime and 154 of chloride of potassium with 100 water, the operation being performed in close leaden tanks, heated by steam, and provided with agitators. A man-lid through which the tank can be cleansed or repaired, and one or two wide tubes descending nearly to the bottom of the vessel, through which materials can be introduced, complete the arrangement. During the action, the temperature rises to about 200° F. After the completion of this operation, the liquid is filtered and evaporated nearly to dryness by steam heat; and the resulting mass is redissolved in hot water and set to crystallize.

The whole of the chloride of calcium remains in the mother-liquors, and the crystals of chlorate are rendered fit for the market by slight washing and draining. The reaction upon which this operation depends is represented by the following equation:—

$$KCl + 6CaO + 6Cl = KO.ClO^{5} + 6CaCl$$

In this process, 154 parts KCl give more than 200 parts KO. ClO^5, while, by the method of direct saturation, 115 parts caustic potash yield only 30 parts of that salt; at the same time, no by-product is formed except chloride of calcium, a substance whose value, even if it were susceptible of no economical application, would be a matter of little consideration to the manufacturer. The uncrystallizable mother-liquors of this manufacture consist, within 1 or 2 per cent., entirely of this salt, and may be decomposed either by an addition of sulphate of potash or of carbonate of soda. In the former case, sulphate of lime is precipitated, available in the manufacture of papers, while chloride of potassium remains in solution, and may be recovered by evaporation, to be employed in the preparation of fresh portions of chlorate; in the latter, carbonate of lime, the "creta præcipitata" of the druggist, is precipitated, and is largely employed by the pharmaceutist and the perfumer. Nearly the whole of the waste liquors of the English manufacturer are converted into the latter product.

The chlorate of potash of the best makers is a nearly pure product, producing little or no precipitate with nitrate of silver or chloride of barium, a condition resulting only from careful attention to manufacturing and manipulatory detail.

The very large quantity of oxygen contained in this substance, and the well-known violence of its deflagration with combustible materials, suggested the possibility of its advantageous application to the making of gunpowder. The result, however, was wholly unsatisfactory, its employment being precluded by the excessive rapidity of the combustion, which even the introduction of a large proportion of nitrate of potash into the composition, failed to control, the essential condition under which the maximum projectile power of an explosive mixture is obtained, being in fact that of an accumulative, not an absolutely instantaneous production of gases. The latter condition is obtained by the introduction of any considerable proportion of chlorate into the mixture, with a corresponding risk of the bursting of the weapon, while an equally fatal objection to its use is the ready explosibility of the powder under slight accidental friction.

Before the introduction to general use of the "lucifers," now so familiar to everyone, considerable quantities of chlorate were employed in the manufacture of matches, which were ignited by applying their extremity to substances charged with sulphuric

acid. The following were mixtures employed for this purpose :—

60 parts chlorate of potash,
14 „ sulphur,
14 „ gum benzoin,

with a little tragacanth and cinnabar.

Or, 30 parts chlorate,
10 „ sulphur,
8 „ sugar,
5 „ resin,

and colouring-material at discretion. The sulphur to be always well wetted before mixture, to avoid risk of explosion.

We may here refer to the use of chlorate as a frequent ingredient in the composition of the most brilliant pyrotechnical mixtures. The following are examples:

Crimson light.		*Green light.*	
Dried nitrate of strontia,	40	Nitrate of baryta . .	77
Chlorate potash,	6	Chlorate of potash .	8
Fine charcoal,	2	Fine charcoal . . .	3
Sulphur . . .	13	Sulphur	13

Purple light.

Crude oxide copper	12
Chlorate potash	30
Sulphur	12

Chlorate of baryta, we may remark, has recently become the subject of attention at the hands of the chemical manufacturer, in consequence of its increasing application as an ingredient in fireworks. It is formed by passing chlorine through a thick milk of carbonate of baryta at a temperature of 200° to 212° F., whereby the whole mass is transformed into a mixture of chlorate of baryta and chloride of barium.

The lucifer matches now universally in use and kindled by simple friction, are tipped with a composition containing a small quantity of chlorate and of phosphorus, mixed up with ground glass and various colouring matters into a paste with gum.

A further consumption of this salt is in the manufacture of percussion caps, whose use is equally familiar. The following composition is applied to the interior of the cap in quantities varying from $\frac{3}{10}$ to $\frac{5}{10}$ of a grain. It need hardly be added that

the manipulation of these dangerous mixtures demands extreme care, and cannot be performed, with any degree of safety, except by maintaining them in a state of constant moisture until the final desiccation of the finished article.

Composition for Percussion Caps.

Chlorate potash	26
Nitrate „	30
Fulminate of mercury	12
Sulphur	17
Ground glass	14
Gum	1

Chlorate of potash has further acquired considerable importance in our manufacturing districts from its application as an oxidizing agent in heightening the intensity of "steam colours;" nor should the subject be dismissed without a passing reference to the value of this salt as an agent of constant value in the laboratory. Finally, as an article of pharmacy, it possseses some interest, being used in considerable doses by the physician, particularly in the treatment of cases of irritation of the mucous membranes.

In conclusion, we may briefly refer to a series of valuable experiments made some years ago by Professor F. Crace Calvert, with a view to the discovery of a cheaper method of manufacturing the chlorate of potash, if not of some other analogous salt available as a substitute.

The process which appeared from his researches to produce the best results, consisted in passing chlorine into a solution of caustic potash containing hydrate of lime in suspension, the action being assisted by heat; and his attention was further "directed to the best means of producing by this method the largest amount of chlorate of potash, an object at which he arrived by examining the influence of solutions of caustic potash, more or less concentrated, on the quantity of salt produced." The proportions which gave the maximum produce, yielding nearly the theoretical quantity, consisted of a solution of hydrate of potash of 1·110 sp. gr. or containing 10·23 per cent. of real potash (or 102·33 grs. to 1000 fl. grains), to which last quantity of liquid was added 358 grs. of slacked lime. The whole was saturated with chlorine at a heat of about 180° F., and on crystallizing gave nearly the theoretical product.

"It is certainly remarkable," says the author of the memoir, "that there should be a determined specific gravity where the chemical reaction is brought to bear to its fullest extent, or where, in other words, the whole of the potash is transformed into chlorate, while in solutions of greater or less specific gravity a smaller quantity of chlorate is produced, with a corresponding increase of chloride of potassium."

It is necessary to add, however, that, although these experiments excited much attention at the time of their publication, they have as yet borne no practical fruits; nor have those manufacturers who have put the question to the test of experiment on the large scale confirmed the whole either of the results or the inferences of Professor Calvert.

The consumption of chlorate of potash in Great Britain is probably limited to 120 tons per annum; but a considerable quantity is, in addition, exported to America and the European continent.

PHOSPHORUS.

Phosphorus is a singular instance of an article, discovered one or two centuries ago, which, until recently, possessed very little interest but to the professional chemist, and more rarely to the physician; but which by an application dating back little more than 20 years has rapidly become an object of large manufacture, and is now, in the everywhere indispensable lucifer match, carried not merely over the civilized world, but to every land which possesses any commercial intercourse.

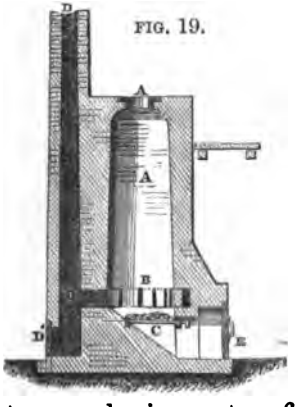
The Dutch chemist, who laboriously first drew it forth in minute quantity, and by a tedious process, from urine, little thought that this substance, so distinguishable from its self-inflaming quality, would, in after time, be manufactured by hundreds of tons, and be not only found in every household, but made the kindling spark of all hearths in every civilized country.

A manufacturer of this article, to whom we are indebted for information on this subject, assures us that a little solitary stick of phosphorus, only 2 inches long, was the whole stock of the chemical establishment in which he was trained. This small sample was the fac-simile of an article he has lived to see pulled

by his own machinery in a cord uncounted miles long, and despatched by the ton together for consumption in both hemispheres, and scattered from Sweden to Spain all Europe over. It is only a few years since we conversed with the chemist in London who first produced it for sale there, for the use of lucifer matches at four guineas per lb. Now, the demand on one hand, and the all-pervading competition of commerce on the other, have reduced it to less than that number of shillings. When we consider the enormous quantity of fuel required (about 100 parts of coal being consumed for every part of phosphorus produced), the immense amount of wear and tear inseparable from the great heat required, and from the nature of the article itself, it is only surprising that so low a price has been attained. We are assured it can hardly be preserved if the increasing agricultural demand for bones and every kind of phosphatic manure should much increase the price of the raw material.

The material for the preparation of phosphorus is bone, or more properly bone-ash—*i. e.*, bone deprived of all its gelatinous parts by calcination. This process, by which the bone is reduced to about half its original weight, is best performed in a furnace so arranged that the combustion can be carried on without interruption. This end is attained by the following arrangement, long used in this country for preparing bone-ashes for the tests in refining lead, and described by M. Payen, in which also the animal matter of the bone is itself made to supply the heat required for the calcination. A (Fig. 19) is a cylindrical furnace, having its upper opening A′ closed by a cast-iron lid. Near the bottom are a number of channels B connecting the body of the furnace with a circular gallery, which terminates in the chimney D. Grate-bars supported by transverse bars, are fixed at C at the commencement of the operation, and the door E being opened, the grate is charged with fuel, which is set on fire from below. As soon as the fire is well burnt up, the door E is shut, and a bundle of straw or shavings set on fire in the lower part D′ of the chimney

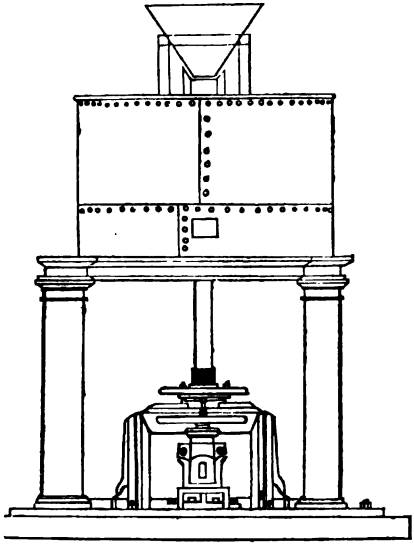
FIG. 19.



in order to establish a draught. The aperture D′ is then closed, so that the flame of the fire may pass through the channels B into the circular gallery, and thence into the chimney. The charge of bones is now gradually introduced by the upper aperture A′, the combustion being thus fed by the animal matter of the bones, and extending regularly from below upwards. As soon as the furnace is full, the aperture A′ is closed for a while, and the bars C are withdrawn, so that the burnt bones at the bottom of the furnace may fall down upon the sloping hearth. The door E is then closed, the furnace again filled up at A′, and in this manner the process is continued. The residue of the operation is a white earthy mass containing 80 to 82 per cent. of basic phosphate of lime, 15 to 17 of carbonate, and 2 to 3 of sand, clay, common salt, &c.

The burnt bones are now to be ground to fine powder in a mill, a simple form of which is represented in Fig. 20. The powder is then passed through a sieve, and digested with a quantity of sulphuric acid rather more than sufficient to convert the subphosphate of lime into superphosphate, that is to say, 100 lbs. of sulphuric acid of 1·550 sp. gr. (equivalent to 66 parts of the concentrated acid) to every 100 lbs of bone-ash. The mixture is made in a large wooden vessel lined with lead. 20 gallons of boiling water are first poured in, then 40 lbs. of sulphuric acid of 1·550, and into this liquid 40 lbs. of the pulverized bone-ash are introduced and well stirred about with a wooden spatula. Brisk effervescence ensues, arising from the decomposition of the carbonate of lime; and as soon as this has ceased, boiling water, sulphuric acid, and bone-ash are again introduced in the same quantities as before; and the same operations are repeated twice more. The vessel then contains 160 lbs. of bone-

FIG. 20.



ash decomposed by an equal weight of sulphuric acid of 1·550. The mixture is kept hot for 24 hours, and stirred from time to time to facilitate the action, then left at rest for another 24 hours, after which the clear liquid is drawn off through a leaden pipe terminating in the upper part of the digesting vessel, into the filters, and thence into leaden evaporating basins.

The deposit in the digesting vessel, consisting of sulphate of lime with a little undecomposed phosphate, is next stirred up with a quantity of water equal to the first, then left to settle; and the weak solution thus obtained from one deposit is passed successively through five or six other similar deposits till it attains a density of 1·076 to 1·093; or, instead of washing by decantation, the liquid may be filtered through a series of vats having false bottoms perforated and covered with cloth.

The solutions of superphosphate of lime thus obtained are concentrated to about 1·206, then transferred to leaden basins, in order that the sulphate of lime in the liquid, which has been rendered insoluble by the evaporation and cooling, may settle down. The clear liquid is then again decanted and passed through a linen filter, after which it is evaporated to 1·308, again left to settle, and filtered. The sulphate of lime deposited in the above process forms a bulky secondary product, which, after drying, finds its way to the manufacturer of artificial manure.

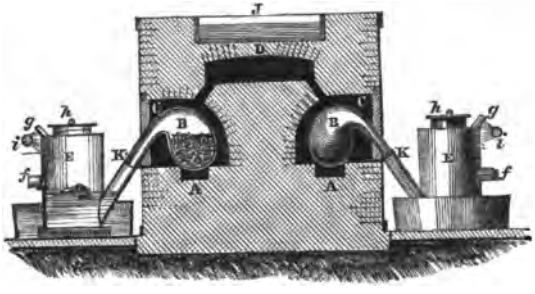
The liquid superphosphate of lime is now concentrated by evaporation to a syrup of about 1·500, and, after cooling, has much the appearance of stiff honey. To this "paste," as it is often called, is added a proportion of about 52 per cent. of finely ground charcoal. This mixture may be then dried by a strong heat applied to the under surface of suitable iron vessels or in a reverberatory furnace. It requires great attention to perform this operation successfully, and much depends on its due performance and on the material being brought into a very dry condition before being put into the retorts.

The retorts in which this "black powder" is now placed are variously made, both as regards shape and size; they are generally made of fire-clay, and may be either cylindrical or globular; many contain as much black powder as will yield from 4 lbs. up to nearly 30 lbs. of phosphorus. They are equally variable in their duration; some manufacturers employing them only once, while those made by others last for several distillations. The furnace in which the retorts are arranged varies necessarily

with the retorts themselves; ten, twelve, or more may be ranged to take the action of one fire.

The retorts are so placed that the mouths of one half of the set open on different sides of the furnace. Fig. 17 represents the arrangement of the furnace when globular retorts are used. Each range of four or five retorts is heated by a fire-place situated below and in front of the channel A; the flame completely surrounds the retorts, and the products of combustion pass upwards into the arched flue D, by which they are conveyed into the central chimney. A leaden basin F resting on plates of cast iron serves for the concentration of the solution of superphosphate of lime, and at the same time prevents the top of the furnace from getting too hot.

FIG. 17.



The neck of each retort passes into an adapter K which itself fits into the upturned neck of the receiver E. Both these joints are very carefully luted with a mixture of dry potter's clay and linseed oil, or of slaked lime, iron filings, and flowers of sulphur made into a paste with blood. The receivers E are made of copper or earthenware, having large mouths, wide enough to admit the arm, and closed by lids *h*. A small tubulus *g* is either left open for the escape of gas, or connected with a gas-pipe common to all the receivers and serving to convey the gases to one point, at which they take fire spontaneously, and burn with a flame several inches in length, sufficient at night to render any other illumination unnecessary. Another lateral opening *f* serves to prevent the water in the receiver from rising above a certain height.

All the retorts being thus arranged, the apertures C are closed with loose bricks or stones; the fire is lighted and the heat very gradually raised so as not to endanger the retorts. As the heating proceeds, hydrogen and carbonic oxide are first given off by the action of the charcoal on the water contained in the acid phosphate; afterwards, when the phosphoric acid itself begins to decompose, the phosphoretted hydrogen appears amongst the

evolved gases, producing white fumes when burnt. Phosphorus now begins to pass over and drops down to the bottom of the water in the receiver. The heat must then be increased more and more till the evolution of phosphorus ceases altogether, which usually happens in about 60 hours or 3 days and 2 nights. The heat required is so great that the sides of the furnace and its iron bracings become red-hot even when they are exposed to the air.

To prevent the neck of the receivers being stopped up, which is particularly apt to occur towards the end of the operation, when the phosphorus comes over in a somewhat impure and less fusible state, containing carbon and perhaps silicon,—it is advisable to clear it out frequently with a bone spatula or iron ladle introduced through the mouth *h*. In performing this manipulation, the hand should be covered with a long glove of chamois leather well moistened with water. The same precaution should be taken in forcing below the surface of the water, the portions of phosphorus which first come over and float at the top, being buoyed up by the gases mechanically enclosed within their substance.

To prevent the water in the receivers from getting too hot, cold water may be added from time to time. A better plan, however, is to place them all in a trough, as shown in the figure, and project cold water on their outsides from a tube *i* connected with a cistern and provided with orifices for the purpose.

Purification of the Phosphorus.—As soon as the distillation is finished, the adapter K is withdrawn and plunged into cold water, and the phosphorus is removed from the receivers. It has several adhering impurities, such as charcoal and oxide of phosphorus, from which it may be freed either by distillation, or straining by filtration.

a. The crude phosphorus is distilled from a cast-iron retort, the neck of which only just dips under water contained in a flat earthen pan, which is so full that, as the phosphorus distils over, some of the water runs over the edge. The phosphorus to be distilled is cut in pieces under water, then mixed with wet sand and put into the retort in quantities of 10 or 12 pounds. The wet sand serves to prevent the ignition of the phosphorus during its introduction into the retort. The application of heat to the retort requires great caution. In the first instance, the water adhering to the phosphorus evaporates and drives out a portion

of the air, then bubbles of gas issue, sometimes igniting as they escape into the air, and lastly drops of phosphorus pass over and condense in the neck of the retort. From this time, the heat must be kept up uniformly, until no more phosphorus comes over; since, if the heat is allowed to decrease, air or water may get into the retort and give rise to explosions. During the distillation, the water in the receiver is kept cold, and the phosphorus is removed from time to time by an iron ladle, so that, in the event of an explosion, phosphorus may not be ignited and thrown about.

b. The crude phosphorus is melted under water at 60° C (140° F.), then left to cool, and, after solidification, wrapped up in moist chamois leather, which is made into a bag *c* (Fig. 18) and immediately plunged into a copper cullender fixed in the middle of vessel A containing water at 50° C. (122° F.) As soon as the phosphorus is completely melted, pressure is exerted on the bag by means of the wooden capsule D D, attached to the lever G G, and the phosphorus is forced through the chamois leather and collects at the bottom of the vessel.

A safer and more complete mode of purifying phosphorus is to filter it while hot through granulated animal charcoal. The charcoal is placed on a layer about 3 inches thick on the per-

FIG. 18.

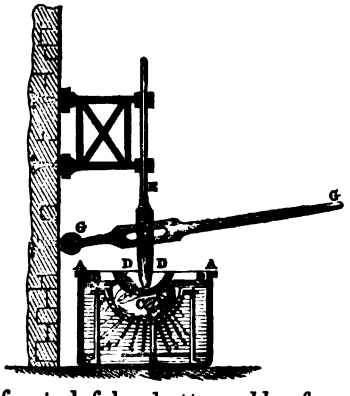


FIG. 19.

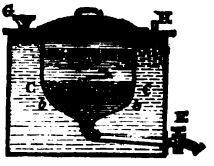
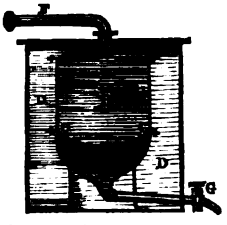


FIG. 20.



forated false bottom *bb* of a cylindrical vessel A (Fig. 19) two-thirds filled with water at 140° F. The phosphorus forms a liquid layer at the bottom of the water, filters spontaneously through the layer of charcoal, and passes through the false bottom to D,

whence it runs through the tube E into another vessel B (Fig. 20) connected with the former by the tube F, the communication between the two being opened and closed at pleasure by means of the cock E. The vessel B likewise heated by a water-bath D D, has a perforated false bottom C C, covered with chamois leather.

The vessel B being filled with water, and the communication opened, the phosphorus runs through the tube F, and settles down on the chamois leather. The tube F is then detached from E and connected with a forcing pump, which forces warm water into the vessel B, and thereby drives the phosphorus through the chamois leather and the false bottom. It then runs through the tube G into a lower vessel containing water. It is thus purified without danger and without loss.

Moulding.—This operation is generally performed by drawing the melted phosphorus into glass tubes with the mouth, care being taken to keep the upper part of the tube full of water. The upper end is then closed with the finger, and the tube containing the phosphorus is transferred to a vessel containing cold water, where it solidifies and contracts in cooling: it is then withdrawn from the tube in the form of a cylindrical stick. This mode of proceeding, however, is sometimes attended with terrible accidents, in consequence of unskilful workmen drawing up the phosphorus into their mouths, where it immediately takes fire.

An easier and safer method is to liquify the phosphorus with water in an elliptical or conical vessel I (Fig. 21), immersed in a water-bath H, the temperature of which is kept exactly at the melting point of phosphorus (44·2 C. or 111·5 F.) At the bottom of this vessel I, is an elbow-tube terminated by a stop-cock J, which is soldered into the side of a vessel L L containing water. A straight glass tube M M′ being inserted into the socket of the stop-cock, and the cock opened, the phosphorus runs into the tube and solidifies: the tube is then detached, the outer extremity M′ being closed with the finger or with a cork, and transferred to a vessel of cold water, where it is removed from the tube, which is then replaced. Or better: The tube M M′ is permanently attached to the stop-cock, and to the cork N is attached

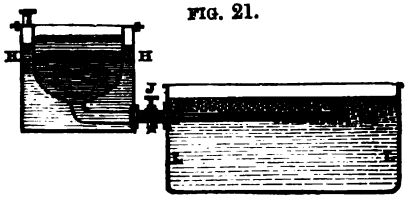


FIG. 21.

a copper wire, which is thrust a little way into the tube. As soon as the phosphorus has solidified round the end of this wire, the cork is withdrawn, and carries with it a cylinder of phosphorus. If then the cock J be left open, the phosphorus will continue to flow into the tube and solidify, and may then be continuously drawn out in a long cylinder, which may afterwards be cut into sticks of any required length.

The same apparatus may be used for the granulation of phosphorus. For this purpose, the vessel L L is filled with cold water only to the lower bend of the tube M M′, and upon it is carefully poured a layer of warm water, a thin board being interposed to prevent the warm water from at once mixing with the cold. The warm water being lighter remains on the surface; and on opening the cock J to a moderate extent the phosphorus flows to the end of the tube and falls out in successive drops, which solidify in passing through the cold water and collect at the bottom in grains. This form of phosphorus is much more convenient for many purposes than the sticks, as it saves the trouble of cutting. To the larger manufacturers of lucifer matches, the phosphorus is often sent in solid masses or cheeses.

The preceding description will suffice to give an idea of the series of processes generally adopted for the manufacture of phosphorus. Several modifications have, however, been proposed, chiefly with the view of economizing material and fuel.

Considerable saving of fuel may be effected by arranging the apparatus in such a manner that the retorts and receivers may be emptied and filled without putting out the fire. This end is attained in the process patented by E. C. Mantrand,* which is also applicable to the preparation of phosphorus from many materials and waste products, which are not sufficiently rich in phosphorus to be worked by the ordinary process.

This process is based chiefly on the reaction which takes place when hydrochloric acid gas or chlorine is brought in contact with a mixture of a phosphate and carbon at a bright red or a white heat. With phosphate of lime and hydrochloric acid, the reaction is—

$$3CaO.PO^5 + 8C + 3HCl = 3CaCl + 8CO + 3H + P;$$

and with chlorine:

$$3CaO.PO^5 + 8C + 3Cl = 3CaCl + 8CO + P.$$

* May 25th, 1854, No. 1166.

In both cases, phosphorus and carbonic oxide are given off, and chloride of calcium is left behind in the retort.

The process is applicable to all matters containing phosphates, but more particularly to those containing phosphate of lime, such as bones, the residuum in the manufacture of glue from bones, the animal charcoal employed in sugar refineries, the residuum of the ordinary manufacture of phosphorus, &c. It is performed by means of ovens, muffles, retorts, or other suitable recipients of fire-clay, or other suitable material permitting of bringing the above-mentioned mixture of the phosphate and carbon to a bright red or white heat, and allowing the passing (for decomposing the phosphate) of a current of hydrochloric acid gas or chlorine through the mixture without attacking the said recipients. The arrangement of these apparatuses is shown in the following figures.

FIG. 22.

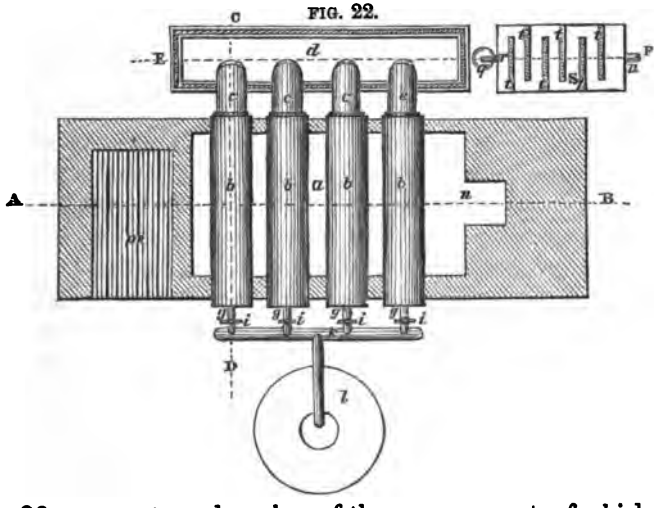


Fig. 22 represents a plan view of the arrangement, of which Fig. 23 indicates a longitudinal vertical section over the line A B of

FIG. 23.

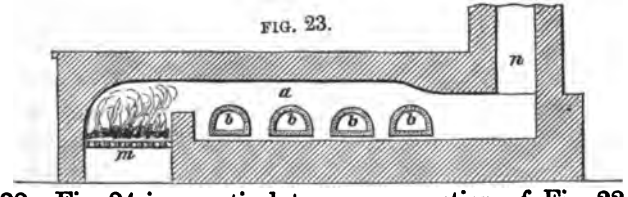


Fig. 22; Fig. 24 is a vertical transverse section of Fig. 22 over the line C D; and Fig. 25 another vertical section over the line E F. It is constructed somewhat like a reverberatory furnace *a*,

provided with one or more muffles or retorts *b*, of fire-clay, or any other suitable material, the ends of which retorts protrude on both sides beyond the oven. At one of these ends a removable slanting tube or adapter *c* is luted, the other end of which passes through the cover *d* of a condenser or tank *e*, lined with lead and partly filled with water, in which the lower end of the adapter dips for about 1 to 1½ inches. The cover *d* dips into a groove *f*, arranged all round the border of the tank, in which groove water is contained in such manner as to form a hydraulic closure for the tank. At the other end of each retort *b* is fixed a tube *g*, communicating by means of a stop-cock *i*, with a main-tube *k*, which latter communicates by means of a pipe with the apparatus *l*, for evolving the hydrochloric acid gas or chlorine, or with any other apparatus from which these gases may be obtained. *m* is the fire-place of the furnace, and *n* the chimney of the same. The muffles or retorts *b* are to be placed in such a position as to incline towards the hinder part, in order that the liquid chloride of calcium or other residue may collect in this part, which is provided with a hole, by means of which the residues may be removed whenever the plug *o*, with which the hole is closed, is removed. *p* is a small tube for conducting the phosphoretted hydrogen evolved during the process under a bell *q*, communicating by means of a tube *r*, with a second tank *s*, also lined with lead, and partly filled with water, and provided with partitions *t*. The phosphoretted hydrogen evolved during the process is ignited at the end of the tube *r*, under the bell *q*, in contact with the atmosphere, by which means phosphoric acid will pass over into the tank *s* along with oxide of carbon formed during the process; the phosphoric acid will dissolve in the water of the tank, from which it may be obtained afterwards by evaporation, and transformed into phosphorus by deoxidizing with charcoal in retorts at a proper degree of heat. The oxide of carbon escapes through the pipe *u*.

FIG. 24.

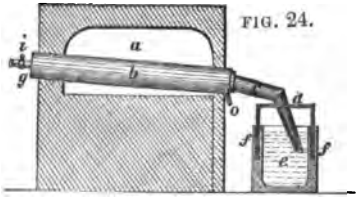
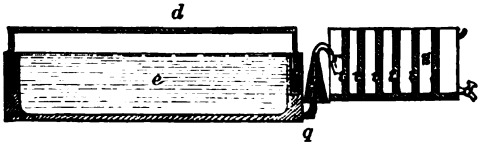


FIG. 25.



The apparatus being thus arranged, the fire is lighted, the

adapters *c* removed from the retorts, and these latter filled with the mixture of phosphatic matters and carbon; the adapters *c* are then fixed again in the back of the retorts, and the joints having been carefully luted, the retorts are brought to a bright red or white heat, when the cocks *i* being opened, the hydrochloric acid gas or chlorine is allowed to pass through the mixture in the retorts, when decomposition will at once begin, and the phosphorus, along with some phosphoretted hydrogen and oxide of carbon, will distil over. The phosphorus will condense in the tank or condenser *e*, and is gathered and afterwards purified in the ordinary manner; whereas the phosphoretted hydrogen is decomposed in the bell apparatus, and the oxide of carbon escapes, as has been already described. When the mixture in one of the retorts is sufficiently deprived of its phosphorus, the stop-cock *k* is turned, and the hydrochloric acid gas or chlorine prevented from entering any further into this retort; the chloride of calcium, forming a residuum in this latter, is permitted to flow out by removing the plug *o;* after which this latter is again replaced in the hole, and the retort being filled with a fresh quantity of the mixture of phosphate and carbon, and the joints having been carefully luted, the cock *i* is again opened as soon as the matters in the interior of the retort have become sufficiently heated, whereby the hydrochloric acid gas or chlorine is allowed to flow into the retort, when the decomposition and the evolving of phosphorus will begin at once. Hydrochloric acid gas is preferable to chlorine.

The carbon to be mixed with the phosphatic matters is pulverized wood charcoal, the quantity being regulated according to the atomic proportion of phosphorus contained in the phosphatic matters, and differing consequently according to their nature; but it is best to use rather a little more of the carbonaceous matters than would correspond with the quantity necessary in conformity with the atomic proportions for deoxidizing the phosphoric acid formed; these proportions generally vary from about 20 to 50 per cent. by weight of the phosphatic matters. The phosphates are reduced as much as possible to a finely pulverized state, and they must be thoroughly mixed with the pulverized wood charcoal; when acting on matters containing phosphate of lime, it is generally preferable to mix with them a certain quantity of silicious sand, and a sufficient quantity of water, in order to allow of forming the entire into small balls, which,

after having been dried, are introduced into the retorts. The reason for introducing silicious sand into the mixture of phosphate and carbon is: first, to divide the particles and augment the points of contact for the hydrochloric acid gas or chlorine to act upon; and, secondly, to neutralize part of the lime from the phosphate of lime, by forming silicate of lime, by which means less hydrochloric acid is required for saturating the remaining lime.

The production of phosphorus may be rendered more economical by combining it with the preparation of gelatine and other products obtained from bones.

Fleck* digests broken bones from which the fat has been separated as completely as possible, in dilute hydrochloric acid, by which means chloride of calcium and acid phosphate of lime ($CaO.2HO.PO^5$) are produced. When the calcareous substance is completely extracted, the cartilaginous mass is washed, immersed in lime-water, again washed, and used for the preparation of gelatine. The solution is evaporated in earthen pans, till its specific gravity is about 1·4, and then run off to cool. The acid phosphate of lime which crystallizes is separated from the mother liquor and pressed between cloths, or spread upon a porous slab, from under which the air is exhausted, and by this means the adherent mother-liquor is separated. The phosphate then appears as a white, gritty powder, with pearly lustre. The residual phosphoric acid is separated from the mother-liquor as phosphate of lime, by precipitation with milk of lime.

The dry acid phosphate is then warmed and mixed with one-fourth of its weight of charcoal, and the mixture is sifted and introduced into the retorts. Fleck recommends for the distillation the use of clay cylinders, like gas-retorts. The discharge-tubes of five of these cylinders terminate in a receiver shaped like a muffle, and placed in a channel, through which water flows. A second receiver is connected with that in which the discharge-tubes terminate. If the mother-liquor, containing chloride of calcium, has not been well separated from the acid phospate of lime, hydrochloric acid is produced during the distillation, and the amount of phosphorus obtained is proportionately less. The mixture of neutral phosphate of lime and charcoal remaining in the retorts is incinerated upon iron plates, heated by the fire used in the distillation; the remaining phosphate of lime is

* Polytechn. Centralblatt, 1856, p. 681; Pharm. J. Trans. xvi. 173.

mixed with that obtained from the mother-liquor of the acid phosphate, and treated as above described, so as to convert it into acid phosphate. The cartilaginous substance is covered with water and heated by steam, till the solution is sufficiently concentrated. By this method, fresh bone yields from 6 to 7 per cent. of phosphorus, and from 10 to 20 per cent. of gelatine; whereas, by the methods formerly adopted, the phosphorus amounted to only 4 or 5 per cent.

Gentele* suggests that the production of phosphorus may be advantageously combined with that of glue, sal-ammoniac, and ferrocyanide of potassium.

The raw materials for the preparation of ferrocyanide are to be charred in the ordinary manner, and the liquid, as well as solid carbonate of ammonia, obtained at the same time, is to be used for making sal-ammoniac.

The separation of the fat from the bones is best effected by boiling them with water. The fat thus obtained serves for making soap. The bones are from time to time taken out of the water by means of rakes, and fresh bones put in, till the liquid becomes glutinous. This product may, according to circumstances, be used as manure or for feeding pigs.

The phosphate of lime is then separated by digesting the bones in hydrochloric acid (sp. gr. 1·03 to 1·05) till they become soft and transparent. Fresh bones yield the largest amount of fat, and also of gelatine; in old bones the gelatine is, for the most part, decomposed. Even in fresh bones, the amount of gelatine varies very much, some containing 45 per cent., others only 30, or even less.

The bones from which the phosphate of lime has been extracted by hydrochloric acid, must be well washed with water, and lastly with lime-water. The gelatinous residue is dried in the air, and then exposed to the action of steam in a well-closed vat, furnished with one or more perforated false bottoms. After a short time, a stream of liquid gelatine flows out of the vat, sufficiently concentrated to be run into moulds and cut into sheets. When a more dilute solution begins to run off, the remaining lumps of gelatine are taken from the vat and boiled with the thin solutions or with water, until completely dissolved, and the liquid is evaporated and run into moulds.

For obtaining phosphate of lime and sal-ammoniac, two methods

* Dingl. Polyt. J. cxliv. 190; Pharm. J. Trans. xvii. 207.

may be adopted. The solution of phosphate of lime in hydrochloric acid may be precipitated by the crude solution of carbonate of ammonia obtained from the charring of the raw materials used for the production of ferrocyanide. When the precipitate has subsided, the solution of chloride of ammonium is drawn off, and a fresh quantity of the hydrochloric solution is precipitated in the same vat. After repeating this operation several times, the precipitate is washed with water to remove the whole of the chloride of ammonium, and then mixed with some of the hydrochloric solution of phosphate of lime, so as to separate the carbonate of lime mixed with the phosphate. It is, however, preferable to precipitate the phosphate of lime by means of milk of lime, because the hydrochloric solution of phosphate of lime is very dilute, and, in the evaporation of the dilute solution in iron pans, the salt is rendered ferruginous, and the pans are eaten away. But when the solution of chloride of calcium obtained in precipitating the phosphate solution of milk of lime is used for converting the carbonate of ammonia into chloride of ammonium, the solution may be evaporated in iron pans without detriment. The precipitation of the carbonate of lime should be effected in hot liquids, so as to ensure the complete separation of the lime. Effervescence takes place on mixing the liquids, because the carbonate of ammonia contains more carbonic acid than is equivalent to the calcium in the chloride of calcium. The phosphate of lime obtained by precipitating the hydrochloric acid solution with milk of lime contains animal substance. It is dried in porous vessels, and then gently ignited in a reverberatory furnace till it becomes white. In this state, it is better adapted for the preparation of phosphorus than burnt bones, on account of its being more easily decomposed; and as it does not contain any carbonate of lime, there is a proportionate saving of sulphuric acid.

The decomposition of the phosphate of lime by sulphuric acid, the separation and concentration of the phosphoric acid solution, the drying of the mixture of phosphoric acid and charcoal, and the distillation of the phosphorus are effected in the manner already described (p. 144).

R. Laming* first prepares phosphate of ammonia by acting upon bone-earth with sulphuric acid, and combining the phosphoric acid thus liberated with ammonia obtained from gas-liquor, then grinds the phosphate of ammonia, without previous separation of

* Feb. 3rd, 1857, No. 311.

the earthy matter, with half its weight of charcoal, and heats the dried mixture to redness in earthen retorts. At the commencement of the process, ammonia is given off accompanied by other gases, and afterwards phosphorus distils over, which may be condensed and treated in the usual way.

H. Bessemer* obtains phosphate of lime by subjecting iron ores to the action of dilute sulphuric acid, and precipitating the acid liquor with lime. The product thus obtained may be used either as manure or for the manufacture of phosphorus. The iron ore thus purified yields iron free from phosphorus.

At least twelve manufactories of phosphorus now exist in Europe, of which six or more are to be found in Austria and Germany, one in Italy, at least three in France, and two or three in England. It is little more than ten years since the manufacture was introduced into England, all that was consumed before that period being imported, partly from Germany, but chiefly from France. At present large quantities are exported from England to all parts of the continent, even so far into the interior as Vienna.† From tolerably reliable data we estimate the present total production of phosphorus in Europe at not less than 400,000lbs. per annum, of which, if we allow 150,000lbs. to France and Italy, the remainder may be allotted in nearly equal proportions to Germany and England. The proportions of phosphorus employed by the match manufacturers of France and Belgium, and the very large consumption of matches in southern Europe, will explain why so much is produced and consumed there; besides which, France, like England, sends phosphorus to Germany. Of the amount apportioned to England (where ten years ago a very trifling quantity was produced) we can speak with entire confidence. An Englishman who had had some experience of this manufacture attempted it in America. We presume it was the high price of labour and fuel which led to his abandoning the attempt. Regarding the consumption of phosphorus, we estimate that Germany uses at least one-half of the total production.

* Provisional specification, Nov. 13th, 1857, No. 2862.

† In the Report of the Jury of the London Exhibition in 1851, will be found a good deal of statistical and historical information of the extent and progress of the manufacture of phosphorus. Though much of the information there is unquestionably correct, we think that the figures of the statement were not then made up to the date of the report, and that there has been a most rapid extension during the subsequent years.

AMORPHOUS PHOSPHORUS.

This remarkable product was discovered by Prof. Schrötter, of Vienna, about twelve years ago, was first exhibited as an actual industrial product in London in 1851, and is now manufactured by Mr. Arthur Albright, of Oldbury, in Birmingham, who has patented it in England, France, Belgium, and several parts of Germany.

Amorphous phosphorus holds in many respects the same relation to the ordinary phosphorus that the diamond does to charcoal, but exhibits, perhaps, even a more extraordinary difference of qualities. Ordinary phosphorus is crystalline, nearly transparent, of specific gravity 1·83, almost white, perfectly ductile, and has a most peculiar odour. Its affinity for oxygen is so great that it inflames in the air at about 165° F. (74° C.), and may be excited to ignition by friction at a much lower temperature; hence it must always be kept under water. It is perfectly soluble in many menstrua, particularly in bisulphide of carbon. It acts as a deadly poison, not only when taken into the stomach, but likewise in the form of vapour.

If we turn to the phosphorus of Professor Schrötter, we find the following opposite characters. It is amorphous, or destitute of crystalline structure, absolutely opaque, of specific gravity 1·964 at 40° Fah., colour generally dark chocolate-red, verging to a metallic black, and, when newly broken, of a peacock lustre; when pure, it is extremely brittle, almost, if not quite, without odour, and exhibits no tendency to unite with oxygen at ordinary temperatures. It cannot be set on fire by friction or percussion, and bears heating to far above 400° Fah. without taking fire. A striking illustration of its properties may be obtained by immersing a piece of it, which should be tolerably pure and free from sharp angles, in spirits of wine, aud setting fire to the spirit; the liquid will then burn entirely away, leaving the phosphorus untouched. Amorphous phosphorus, after being ground under water, may be dried by a sand-heat over a naked fire, and then sifted. By this treatment, it is obtained in the form of a fine dry powder, which is best preserved in tin cases. Schrötter maintains, indeed, that when pure, it is absolutely unaffected by exposure to the air in a state of very minute division; however, it may, perhaps, be somewhat susceptible of oxidation, and may require exclusion of air and light to ensure its permanency.

Amorphous phosphorus is absolutely insoluble in bisulphide of carbon, and likewise in the animal secretions. It is therefore perfectly innocuous when taken into the stomach. Dr. De Vry,* of Rotterdam, gave 3 grammes (more than 45 grains) of it to a dog without producing any poisonous effect. It is questionable, also, whether a substance so insoluble in the animal fluids, can produce any therapeutic effect; nevertheless, it is used in medicine, and is regarded by some practitioners as a valuable addition to the materia medica.

Preparation of Amorphous Phosphorus.—The transformation of ordinary into amorphous phosphorus is effected by keeping it for 8 to 12 days at a temperature of 280° C. (576° F.) in a close vessel. For the first two days, the temperature must be raised very gradually, and not allowed to rise above 240° C. (504° F.) to prevent the phosphorus from boiling, which it would do if raised to a higher temperature before it had been rendered more viscid and less volatile by a commencement of its transformation. The temperature is then to be gradually raised to 280° C. but not higher, otherwise the amorphous phosphorus will rise in vapour and condense again in the ordinary form.

The following is a description of the process on the large scale as patented by Mr. Albright.† The apparatus is represented in Figs. 26 and 27.

A A is a cast-iron vessel set in brickwork in the ordinary manner of a furnace, having a fireplace beneath of the ordinary construction. From the inside of the flange of this vessel, a smaller vessel B B of the same material is suspended and made fast by means of the screw pins I I, as shown in section in Fig. 26, and by I I I in plan, Fig. 27. The space between the two vessels contains a metallic bath composed of a mixture of tin and lead in equal parts. G is a cast-iron cover to the inner vessel B, fitting the top edge by means of a groove, and fastened to the outer vessel A by the screw pins H H (Fig. 26) and H H H (Fig. 27). A screw F passes through a three-armed iron holder L L, Fig. 27, which is made fast to a third moveable iron vessel C C, placed in a sand bath shown by N N. In the interior of this iron vessel C C, another vessel of glass or porcelain D D is fitted, in which the phosphorus to be operated on is placed. J is a curved pipe of iron or copper, passing freely through the cover G, but screwed into the

* Pharm. J. Trans. x. 497.

† July 17th, 1851, No. 13,695.

cover E, and having an exit at the extremity into a detached vessel K K. This contains mercury or water. If the first is

FIG. 26.

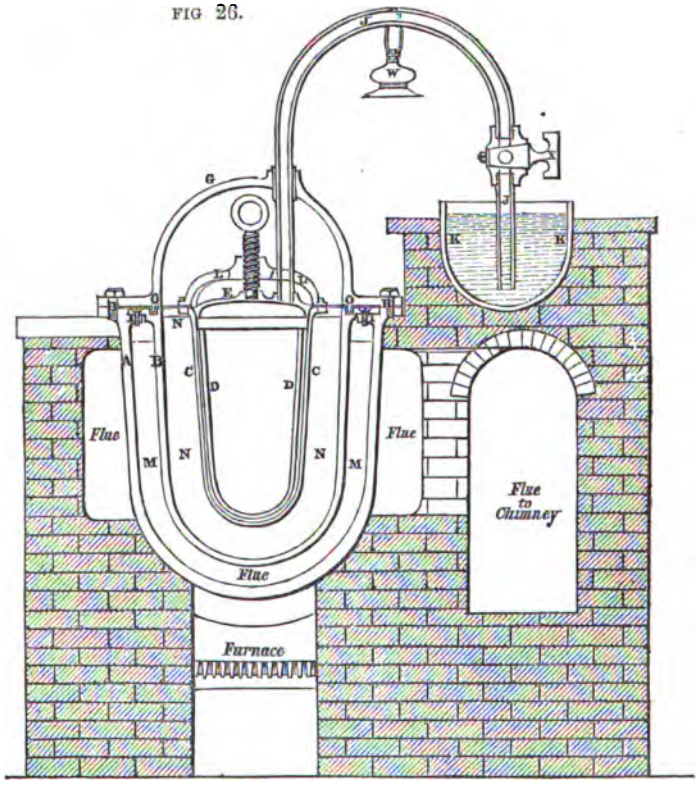
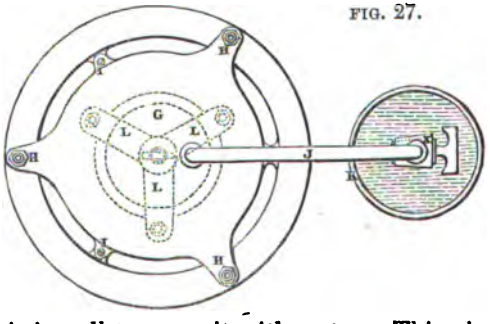


FIG. 27.



employed, it is well to cover it with water. This pipe J acts as a safety valve, as the metal or water in the vessel K K prevents the return of the atmospheric air into the inner vessel C C. W

is a spirit lamp, placed, if necessary, under the pipe J for the purpose of keeping it hot, so that clogging of the pipe by the condensation of distilled phosphorus may not occur. X is a stop-cock to prevent the ingress into C C of the contents of K K, or of the atmospheric air, and should be closed before the apparatus in the furnace is allowed to cool down, or the vessel K K is removed. The cover G is used chiefly as a means of preventing accidents, and is not essentially necessary. Between the end of the screw F and the cover E, a small but strong concave disc or spring of steel should be inserted, and so adjusted as to give a slight play to the cover E in case of violent action arising in the interior, or the stopping up of the pipe J. Neither of these accidents is likely to occur if the operation is conducted with proper attention. The whole apparatus is set in brick work, with suitable furnace and flues for the purpose of heating it and maintaining the temperature required for the process. The phosphorus to be brought to the amorphous state is to be previously melted, cooled under water, and dried as much as possible. The mode of operation is then as follows:—The cover of the inner vessel is to be raised, the phosphorus deposited, and the covers E and G replaced. A fire is then made under the outer vessel A A, and the temperature raised to such a degree as shall be sufficient to drive off the air, and also the gases which may be generated in the interior vessel, which will escape at the exit of the pipe J, dipping into the vessel K K, covered with mercury or water, as before described. The action of water in the vessel K K, when mercury is employed, is useful in order that any phosphorus which may distil over and pass down the pipe J may be covered by it. The temperature is to be gradually raised until bubbles escape at the end of the pipe J, taking fire as they enter the air. When these bubbles have escaped freely for a time, the temperature may be raised to 500° Fah. In order to judge of the temperature, a thermometer is placed in the metallic bath. The temperature must be maintained for a certain time,—the length of which depends so much on accompanying circumstances that it can only be determined by experience,—at a point within a few degrees of the before-mentioned elevation, perhaps rather higher than lower. So soon as the phosphorus is brought to the amorphous state, the vessel may be allowed to cool down. The phosphorus is then taken out, to effect which it may be necessary to break the glass or porcelain vessel. It may be desirable to

increase the pressure on the vessel C C and D D; and for this purpose the vessel K K should be deepened, so as to contain more mercury, and by this means a pressure of an atmosphere or even more may be gained. In this case it will be necessary to remove the disc or spring so soon as the steam and fiery bubbles which arise in the first part of the process have ceased to appear at the end of the pipe J. The phosphorus is then to be levigated under water, from which it may be drained by being placed in a bag or on a filter. If the operation has been successfully conducted, the amorphous phosphorus produced contains only very slight traces of common phosphorus. The levigated phosphorus, while moist, should, in order to purify it, be then spread thinly, for convenient working, on separate shallow trays of sheet iron or lead; and these trays can be so placed alongside each other as to receive the heat of steam, or of a heated bath of water, or of chloride of calcium, or of sand, or of each consecutively in this order; but whichever be employed, the temperature must be raised gradually and the phosphorus frequently stirred until the disappearance in the dark of all luminous vapour shall show that the whole of the adhering crystalline phosphorus has become oxidized. The operator should have water at hand to quench any fire that may arise before the whole mass has perfectly oxidized. When the process of purification is thus far completed, the phosphorus must be washed until the water in which it is so washed shows no trace of acid when tested. In case the amorphous phosphorus produced contains too large a proportion of the unconverted phosphorus, bisulphide of carbon or other solvents may be employed to wash out the ordinary phosphorus.

Uses of Phosphorus.—The chief use of phosphorus is for the preparation of lucifer matches, for which purpose both the ordinary and the amorphous varieties are used. Ordinary phosphorus is also used in the formation of composition for poisoning rats and black beetles; and both kinds are employed in a variety of ways in chemical and pharmaceutical preparations.

A phosphorated paste for poisoning rats may be prepared by dissolving 250 parts by weight of gum arabic in 500 parts of water at 140° F., then adding 15 parts of phosphorus, stirring as the phosphorus melts, then removing the vessel from the fire and continuing the stirring as the mixture cools, in order to thoroughly incorporate the phosphorus. The mixture is then again placed over the water bath, the stirring being still continued; a

paste previously made up with 100 parts of flour or potato-starch * and 160 parts of water is added to it; and the whole is beaten up for half an hour, the temperature being maintained at 122° Fah., after which it is left to cool, the agitation being still continued till the temperature has fallen to 86°. The process yields from 500 to 550 parts of phosphoretted paste. To effect a still finer division of the phosphorus, the paste when cold is ground under the muller; it is then preserved in close vessels.

The best way of using the paste for poisoning rats is to spread it on two slices of bread laid together by the covered surfaces, so that the paste may not be seen. For black beetles, it may be spread on small pieces of paper, placed about the floor at night.

The following formulæ are also used:—

Paste officially recommended in Prussia.

Finely divided phosphorus	8	grammes
Rye-flour	180	„
Tepid water	180	„
Melted butter	180	„
Sugar	125	„

Pâte de Dubois.

Phosphorus	20	grammes
Warm water	400	„
Flour	400	„
Nut-oil	200	„
Pounded sugar	250	„

LUCIFER MATCHES.

The history of the lucifer match, together with that of the earlier contrivances for producing fire, has already been given in this work (vol. i. part 2, page 753). We have now to treat of the present stage of the manufacture, especially with reference to the use of amorphous phosphorus, and likewise of the machinery used for cutting and dipping the matches.

* Potato-starch is for the most part preferable to the flour of wheat or other grain because it is not liable to ferment.

Ordinary lucifer matches are simply wooden sulphur matches tipped with a paste containing phosphorus, and capable of igniting by friction. The materials added to the phosphorus to promote its ignition are chlorate or nitrate of potash, or certain metallic oxides which easily give up their oxygen, such as the peroxides of lead and manganese. Chlorate of potash causes the paste to ignite with detonation when rubbed, and often occasions the projection of a portion of the burning matter to a considerable distance. This projection, which is rather dangerous, may be prevented by using nitrate instead of chlorate of potash; the matches then burn quietly. The phosphorus and the salt or oxide which is to supply it with oxygen for combustion, are made up into a paste with a strong solution of glue or gum, a small quantity of vermillion or Prussian blue being added as colouring matter, and sometimes a little fine sand to increase the friction.

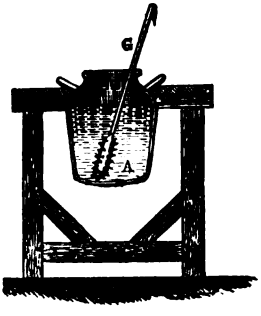
The proportion of phosphorus varies considerably, being sometimes as high as 30 or even 50 per cent., and sometimes as low as 10 or even 5 per cent. The following are two compositions recommended by Böttger in 1844, and still in use for the preparation of noiseless lucifers:

Phosphorus (ordinary) . .	4	. . . . .	9
Nitre	16	. . . . .	14
Red lead	3	Binoxide of manganese	14
Strong lead	6	Gum	16

When glue is used, it is broken into lumps, which are left to

FIG. 28.

FIG. 29.



soften for three hours in cold water, and then melted at the temperature of boiling water. This operation may be performed in a copper digester A immersed in a water-bath B (Fig. 28). When the glue is well melted and of the temperature of 100° C., the vessel A is removed and placed in the circular aperture of the stand G (Fig. 29), which holds it firmly. Phosphorus is then gradually added, which immediately melts, and must be kept constantly covered by the watery liquid; the mixture is stirred with a brush G, the agitation being increased in rapidity as the liquid cools. The nitre or chlorate is then added, together with the sand and colouring matter, and the mixture is kept in the liquid state, by placing the pot over a water-bath at the temperature of 36° C. (97° F.). The paste is then spread uniformly on a table of marble or cast iron, kept at a moderate heat by a water-bath placed below it, the layer being renewed as the dipping of the matches goes on.

When gum is used, the mode of preparing the paste is essentially the same; but the mixture may be spread on the table while cold, and the whole operation is more easily performed. For this reason, gum is much used by the continental makers: but in England glue is preferred, because matches made with gum will not bear the humidity of our climate.

The composition and the sulphur-splints having been prepared, the operation of dipping is conducted in two ways, viz. the *bundle dip* and the *frame* or *clamp dip*. In the former case, the dipper takes a bundle of splints, tied round with string, and grasping it in both hands, causes the ends of the splints, by a skilful movement, to expand into so wide a circle that they become detached, and, on being dipped, each will receive its own separate portion of the composition. By this method, it is the end of the match only which is covered with composition; and from the trifling consumption of material, as well as the cheapness of the labour, this kind of match is the least costly in manufacture. The frame or clamp dip, is however, gradually displacing the bundle dip, at least in this country.

In the other mode of manufacture, the *frames* or *clamps* consist of separate sticks of wood about 15 inches long, 1 inch wide, and ¼ inch deep, one side of which is covered with woollen list, and the other scored with grooves about five to an inch, and each deep enough to receive a splint. A child will rapidly fill a grooved strip with splints; the list-covered side of a second strip

keeps the splints in their places; and by a succession of strips of splints, a frame or clamp is quickly formed, which will hold 1500 or more matches, presenting a surface of about 15 inches square. When well bound together, these frames full of matches are ready for dipping.

The paste is either spread upon tables of stone or metal, as aforesaid, by means of a roller or spatula, or a slight iron frame called a *gauge* is placed on the dipping table, into which the composition is poured, and thus the *depth* of the dip is regulated. The composition is kept at a uniform temperature by a water-bath placed under the dipping table. A workman knows by practice how to manipulate the frame, so as to get out of the same "bed" of composition a succession of frames dipped to any equal depth, until at last the quantity removed has so thinned the "bed" that the gauge must be refilled. In one of the extensive Austrian manufactories, half a dozen workmen, stationed at a row of dipping stones, dip and hand back the frames to the attendant boy with such celerity that they can turn out 20 million matches in a day.

The frames holding (say) 1500 matches are now placed in a horizontal position and allowed to dry for some time in the air. After the lapse of three or four hours, they are removed to a stove, and suspended from iron railings, where they are exposed to a temperature of 80° or 90° Fah., by means of steam or hot water. When glue is used, the desiccation is complete in two hours, but it occupies an entire day when gum is employed as the mucilage. Each set of railings is covered with sheet iron, to prevent combustion spreading in case of fire; and the floor of the stove is kept covered with sand, to the depth of several inches, to extinguish any ignited match as it falls, or any that may take fire by the friction caused by the passing to and fro of the workmen.

As soon as the drying process is complete, the frames are carried to a workshop, where women and children remove the matches, and immediately deposit them in boxes. These work-people have always by their sides boxes half filled with sawdust in which they plunge any match ignited by accident, so as at once to extinguish the flame. They have also at hand large and small cisterns in which to immerse their hands in case of accident.

Special methods of dipping and drying by machinery will be described in the following pages.

Lucifers without Sulphur.—Some matches, instead of being coated at the ends with sulphur, are impregnated throughout with stearic acid or wax. To prepare them, the splints, after being carefully dried, are placed in the usual frames, and the ends are brought for a moment in contact with a red-hot iron plate, so as to become slightly carbonized. They are then dipped into a thin layer of stearic acid or wax, kept in the melted state in a flat-bottomed tinned copper basin, by means of a water-bath. A small portion of the fatty matter is immediately absorbed by the ligneous tissues, and rises by the capillary action of the fibres, impregnating the wood thoroughly to within a short distance of the end.

The paste for dipping these matches requires less gum and a more active oxidizing agent than that for the sulphur-matches. The following are two of the compositions in use :—

Phosphorus (ordinary)	3·0	. . . . .	3·0
Strong glue	3·5	Gum tragacanth . .	0·5
Water	3·0	. . . . .	3·0
Fine sand	2·0	. . . . .	2·0
Vermillion or Prussian blue	0·1 to 0·5		
Chlorate of potash . .	3·0	Binoxide of lead . .	2·0

The binoxide of lead in the second of these compositions may be replaced by a mixture of 2 parts of red lead and 0·5 parts of strong nitric acid.

Matches thus prepared burn more readily than sulphur-matches, because the fatty matter and the wood take fire together, whereas in sulphur-matches the wood does not ignite till the sulphur is nearly consumed. The stearic acid matches also burn with a brighter flame, and are free from the suffocating odour which the sulphur-matches evolve in burning. The extra cost of the stearic acid is compensated by the much smaller quantity required compared with sulphur, the proportion being 1 to 10.

Taper or Vesta matches are prepared by machinery not unlike a weaver's loom with its warp ready for weaving. A number of threads of fine cotton yarn slightly twisted are wound upon a reel, and the ends are passed into a vessel containing melted wax under a rod placed across the pan, for the purpose of keeping the yarns immersed. The fluid wax adhering to the yarn forms the taper, and to render it smooth and equal in thickness, the taper is passed through a small hole in a metal

plate, which acts as a draw-plate, scraping off the superfluous wax. Passing the taper about three times through the melted wax and draw-plate is sufficient to give it the proper substance, after which it is pressed with a wet cloth and passed through the draw-plate for the last time to give it a polish. Rosin and tallow may also be used in place of wax, and essential oils or perfumes may be added to give a fragrant odour. To cut the tapers to the lengths suitable for matches, they are wound upon reels or bobbins of large diameter, and progressively drawn off by a cutting machine of peculiar construction.* The dipping and subsequent operations are the same as for wood matches.

These matches must be tipped with a very inflammable paste; because, having but little rigidity, they cannot bear, without bending, so much friction as the wood matches.

The composition of this paste is as follows:

Phosphorus (ordinary)	12 parts.
Gum	14
Sulphide of antimony	3
Red lead . . 35 / Nitric acid . 21	56, or binoxide of lead 36.
Vermillion	0·1

Fusees for lighting cigars are made from strips of pulp or thin card-board, previously prepared by steeping in solution of nitre. A girl then takes twenty-five strips in her hand, and with a stick shaped like a paper knife, spreads a portion of the red composition over the cut extremities of the upper strip, which is then placed on the table, and so on, till the whole are prepared. Another girl receives these strips, and twists them, so as to separate the fusees from each other, and arranges them on a tray, which, when full, is placed on a rack to dry.

Fusees are sometimes made of small round or lozenge-shaped pieces of prepared paper attached to a thin stem of wood or metal which may be thrust into the end of a cigar, either before or after the fusee is lighted. (See list of Patents at the end of the volume, 1849, No. 12,469, and 1858, No. 2085).

A match or fusee, which will burn with a flame of sufficient persistence to resist the action of the wind, has been invented and

* In Payen's "Chimie Industrielle" (4th ed. ii. 361), it is stated that vesta matches were invented in 1836; but the description above given is extracted from the specification of a patent taken out in England in the name of W. Newton in 1832.

patented in the year 1854, by Messrs. Bardet and Collette. The preparation is thus described:

"We saturate by immersion or otherwise, sheets of paper, cardboard, wood, or any other suitable combustible matter, in a solution of saltpetre, to which solution, if required, can be added a certain quantity of any suitable odoriferous matter, in order that during combustion an agreeable scent may be developed; after being completely dried, we place between any two such sheets a thin layer of any of the phosphorated gummy pastes usually employed for forming the igniting part of friction matches, with which paste has been mixed a suitable quantity of any incombustible substance, such as ground glass, fine sand, pulverized pumice-stone, pulverized calcined alum, or any other similar suitable inert matter, having the power of preventing the combustion from spreading too speedily in the paste from one particle to the other.

"It is necessary that a certain portion of the sheets should be left without paste, in order to form that end of the lucifer match which is to be held in the hand. After a proper desiccation, the two sheets will firmly adhere, and may then be cut in strips of the required size for forming matches, and the whole may then be cut by means of scissors, knives, or any other suitable mechanical agency; after which these strips are covered with varnish, or any other suitable impermeable coating, in order to protect the match from humidity and prevent the evaporation of the phosphorus. To protect them against involuntary or accidental ignition, occasioned by packing or other causes, this coating should extend only to that part of the strips containing the phosphorated paste. It will be found convenient to mix a certain quantity of any suitable colouring matter with the coating, in order to distinguish the combustible part from that which is to be held in the hand. If required, the end of the match may be dipped into phosphorated paste of greater inflammatory power than that contained in the match, to facilitate the lighting. After having been thoroughly dried, they may be packed up in boxes or otherwise."

MATCHES TIPPED WITH AMORPHOUS PHOSPHORUS.

The use of ordinary phosphorus in the manufacture of lucifer matches is attended with certain inconveniences, arising partly from the great facility with which it is set on fire by friction or by

slight rise of temperature, partly from the slow combustion which it undergoes at ordinary temperatures, whereby acid vapours are produced of very deleterious character. From this cause, the workpeople engaged in the manufacture, especially the dippers, who are most exposed to the acid vapours, occasionally suffer from a peculiar disease of the jaw, which commences with pain and swelling, and ultimately produces necrosis of the bone, to such an extent, in some cases, as to necessitate the removal of a large portion of the jaw. The disease appears to have prevailed to a great extent in the early days of the manufacture, and cases of it may still be found, especially among persons who carry on the process in a small way in confined apartments; but in the larger English manufactories, where due attention is paid to ventilation and cleanliness, it is now of rare occurrence. Mr. Letchford, of Old Montague Street, Whitechapel, who has kindly permitted the writer to visit his factory, states that no case of the disease has ever been observed among his workpeople, although some of them have been in the establishment for fifteen years. From Continental manufactories, however, the accounts are less favourable. In a report on the manufacture and use of chemical matches, recently presented to the "Académie Imperiale de Medicine," by MM. Poggiale, Chevallier, and Duvergie,* it is stated that the phosphorus disease is still very prevalent among persons employed in the manufacture, 28 cases having been recently observed at Paris and 12 at Lyons. The same report also states that cases of suicide and of criminal poisoning by means of matches tipped with ordinary phosphorus, are of frequent occurrence in France, and greatly on the increase. For these reasons, and on account of the danger of fire from ordinary phosphorus, the reporters strongly recommend that its use be altogether discontinued in the manufacture of matches, and that its place be supplied either by amorphous phosphorus or by an inflammable composition not containing phosphorus.

The use of amorphous phosphorus is certainly free from all the objections above mentioned. It is not volatile or subject to slow combustion at ordinary temperatures, or even at the heat required to keep the paste in the liquid state, and can therefore never impregnate the air of the factory with poisonous vapours. Moreover, it is not liable to be set on fire by accidental friction;

* Journal de Pharmacie et de Chimie, 3rd series, tom. xxxvii. p. 180. (Mars, 1860.)

neither is it poisonous under any circumstances; whereas ordinary phosphorus, as already observed, is very poisonous, even in the solid state, and instances have occurred of children being poisoned by sucking matches tipped with it.

Notwithstanding these advantages presented by the amorphous phosphorus, it has not come into general use. Some excellent matches made with it were exhibited by Dixon and Co. in 1851, but at present its use appears to be altogether abandoned in this country; indeed, we are informed by Mr. Albright that there is but one match manufactory in Europe in which it is employed, viz., that of Messrs. Coignet, Pinet fils, and Co., of Paris, who make matches on Lundström's principle, presently to be described. The chief objection made to the amorphous phosphorus is the greater cost which it entails; for, as it is much less inflammable than ordinary phosphorus, a larger proportion of it is required to form the igniting composition; it is found that 1 lb. of ordinary phosphorus will go as far as 3 lbs. of the amorphous variety. This objection has peculiar force in this country, where there is a strong prejudice among consumers in favour of matches heavily tipped, known in the trade and in popular phrase as the "hung dip," or "big head." English manufacturers all fear to resort to the simple expedient of reducing the size of the head (which, as shown in the beautifully made Swedish matches, now largely imported, is quite compatible with a perfect match), lest, by running counter to popular prejudice, they should incur loss. On the continent there is another objection to the use of amorphous phosphorus, arising from an exaggerated fear of the use of chlorate of potash, on account of the tendency of mixtures made with it, to explode during the process of manufacture; and it does not appear possible to make an easily igniting match with amorphous phosphorus without the use of chlorate of potash. There may, perhaps, be some danger in the use of chlorate of potash, but, nevertheless, it is in daily use in England on a very large scale.

The paste used for matches tipped with amorphous phosphorus may be made either with gum or with glue. M. Payen gives the following composition:—

Amorphous phosphorus	3		3
Chlorate of potash	4		4
Gum	3	or glue	2·5
Water	3		5
Pounded glass	4		1·5 to 2·0

Mr. Albright, who was the first to introduce the manufacture of amorphous phosphorus into this country, has made certain improvements in the preparation of these matches (patented Sept. 25th, 1856, No. 2249), consisting: 1. In the use of flour paste to cause the materials of which the head of the match is composed to adhere well to the splint; 2. In using two compositions or pastes, one containing chlorate of potash, and the other the amorphous phosphorus, and in afterwards applying to the surface of the heads of matches, according as one or other of the above-named substances has been omitted, a thin coating of amorphous phosphorus, which is made to adhere by a suitable cement,—or chlorate of potash, by dipping the heads of the matches in a solution of that substance; 3. In coating or varnishing the heads of lucifer matches with an aqueous shellac varnish, or with a mixture of white of egg or blood with lime or chalk, to which may be added powdered glass, oxide of iron, and other substances.

The following is the manner of preparing the lucifer match composition, into which the paste of wheat flour enters, and which may be called "the simple amorphous phosphorus cold composition," meaning by cold, that no heat is required in the operation of dipping the matches in it.

2 parts of best wheat flour, and 14 parts of water, are mixed together and boiled into paste. In boiling this mixture into paste, it naturally loses some of its water; care must therefore be taken that it does not become too thick.

Of this paste there are taken	15 parts,
of chlorate of potash in very fine powder. .	6 „
of very finely powdered glass	3½ „
of powdered amorphous phosphorus .	1½ to 2½ „
making	26 to 27 parts.

These materials having been intimately mixed, a small quantity of water is added, if needful, to reduce the mixture to such a consistency as to make it adhere in suitable quantity to the ends of the splints dipped into it. For a sulphured splint, but a small quantity of the composition is needful; for one dipped in stearine, more is required. These matches will remain in good condition so long as they are kept dry.

To harden the composition to enable it better to resist humidity, the following methods are used for the preparation of the flour paste.

First, to the proportions of flour and water above given, there

are added 1 or 2 per cent. of sulphate of alumina (free from potash), and the materials are allowed to repose for half an hour before boiling into a paste; when the paste is made, a quantity of powdered chalk is added equal in weight to that of the sulphate of alumina employed, in order to combine with the acid of the latter.

Or, secondly, the flour paste is mixed with water, to every half pint of which the white of one egg of average size has been added.

Or, thirdly, for half the quantity of water required for the paste there is substituted an equal volume of fresh uncoagulated blood.

Or, fourthly, to obtain a very hard composition, there is added to the pastes Nos. 2 and 3, ½ per cent. to 1 per cent. of chalk, and the same quantity of red oxide of iron, and 3 per cent. or more of a solution of glue, consisting of one-third glue and two-thirds water.

It is desirable to use the best quality of flour, and to pass the paste through a sieve before using it.

To prepare a lucifer match, no phosphorus enters into the first dip, the ignition of which is made to depend on there being afterwards attached to it a small portion of that substance. The two following compositions are used, which may be called B preparatory and B final:

The *B Preparatory* composition is made by mixing together—

5	parts	of very finely powdered glass,
5	„	sulphide of iron,
2	„	red oxide of iron,
30	„	chlorate of potash,
15	„	solution of glue (glue, 1 part; water, 2 parts),
57,		which, if too thick, may bear dilution with 3 parts or more of water, which will make 60 parts more of B preparatory composition.

These materials are perfectly innocuous, in case of the matches being accidentally or otherwise swallowed.

The two preparations of iron, forming together 7 parts of the above composition, may at pleasure be replaced by 5 parts of the red sulphide of antimony, often called crocus of antimony. The composition may also be made somewhat cheaper by omitting the oxide of iron and replacing 5 out of the 30 parts of chlorate

of potash by 10 parts of peroxide of manganese (containing 90 per cent. of real peroxide).

Into a preparatory composition prepared as above described, the sulphured, or stearined, or otherwise prepared splints are dipped in the ordinary manner, the composition being maintained at the needful state of fluidity by means of heat, applied according to any of the usual methods. The dipping operation may be performed without the smallest apprehension of danger from the use of this composition. The matches dipped in them dry rapidly in their frames, and in order to convert them into lucifer matches, they are coated with the B final composition, which is prepared as follows:—

B Final.

Shellac, 7 parts, dissolved in spirits of wine or vegetable naptha, 43 . .	50	parts, by weight.
Powdered amorphous phosphorus . .	50	„
	100	parts.

Or, in place of the above, may be used,—

No. 2 B Final.

Solution of glue (glue, 1; water, 2) .	15	parts, by weight.
Water	40	„
Amorphous phosphorus	20	„
	75	parts, all by weight.

Or,— *No. 3 B Final.*

Shellac			17 parts.
Dissolved in water	120	by weight	123 „
Liquor of ammonia, 880 per cent. sp. gr. 3	3	„	
			140

The above materials are well mixed, and the shellac is dissolved by means of a gentle heat, and then there is added of—

Very fine powdered glass. . . .	20	parts.
Of amorphous phosphorus . . .	50	"
	210	parts, all by weight.

Or,— *No. 4 B Final.*

Russian glue	1⅓
Dissolved in water	21
Very finely powdered glass	12
Red oxide of iron	4
Amorphous phosphorus	7
	45⅓

Two methods are employed for giving the dip or coating of final composition to the once-dipped matches; the first, that of transferring the final composition to the ends of the matches by means of a hollow cylinder of vulcanized india-rubber of about $\frac{2}{4}$ inch thickness, its circumference being one-third more than the length of the frames containing the matches, and its length equal to the breadth of the frames; the second, that of dipping a frame filled with the matches into a very thin bed of the final composition. For both these methods, a shallow tin dish is employed, $\frac{2}{4}$ inch deep, and of an area between that of the frame and that part of it which is occupied by the matches placed ready for dipping. The bottom of the dish ought to be perfectly level, and for use to be also placed on an exactly level surface. When thus made ready, the requisite quantity of the final composition is introduced. A larger quantity will be required where the transfer is to be made by means of the India-rubber cylinder than when it is to be made by dipping. In using the India-rubber cylindrical roller, it is made to revolve in the final composition, so as to coat therewith two-thirds of its perimeter, and then immediately passed over the ends of the matches duly fixed in the frame, thus communicating to them the coating of final composition, in a manner much resembling that by which printer's ink is communicated to the types. It may happen that some of the matches have not been touched, but these should be very few; and this defect is remedied by a morsel of sponge dipped in the composition.

The second mode of coating the matches, that of dipping a frame of them into the final composition, requires no description; the only nicety required is not to empty a needless quantity of composition by having too much in the tin dish.

The above-described method of using amorphous phosphorus

presents the advantage of entirely obviating the danger (especially when heat is required, as in all glue-made matches), which may arise from mingling the amorphous phosphorus and the chlorate of potash in one composition. It has also the advantage of great economy in the very small quantity of amorphous phosphorus required by this method to ignite the lucifer match.

The following is the method of preparing lucifer matches from which chlorate of potash is excluded in the first or preparatory composition.

The sulphured, or stearined, or otherwise prepared splints are dipped into a composition formed as follows, which for distinction may be called preparatory composition C:—

Amorphous phosphorus	2 parts
Powder of pure nitrate of potash .	5 „
Very finely powdered glass . . .	3 „
Solution of glue (glue, 2; water, 1)	6 „
	16 „

The quantity of amorphous phosphorus may be diminished, even to the extent of one-half, by substituting double or treble its weight of sulphide of antimony or other metallic sulphide. This composition requires to be on a heated surface during the operation of dipping the matches. When the matches have become dry or nearly so, they are dipped into a strong or even hot concentrated solution of chlorate of potash in water, which operation may be conducted in a tin dish of the same kind as before described.

As the matches thus prepared do not possess uniformly sufficient excitability, the defect is supplied by redipping the matches which have received a proper quantity of the preparatory composition C, into the following or final composition D:—

Chlorate of potash	20 parts
Very finely powdered glass . . .	17 „
Glue solution (glue, 1; water, 2) .	3 „
Water	12 „
Amorphous phosphorus	2 „
making 54 parts, all by weight.	

It will be seen that phosphorus is not wholly excluded from this composition, but it is so far excluded, that were this composi-

tion to be used alone for heading matches, the matches so formed would not be practically useful.

The patent likewise includes the preparation of aqueous shellac varnish and albuminous mixtures employed to coat the ends of the matches, as also the boxes (of chip or scaleboard) for containing the same.

The aqueous shellac varnish is prepared by adding to any given quantity the one-fiftieth part of its weight of strong liquor of ammonia (880 specific gravity), and the tenth to the sixth of its weight of shellac in coarse powder, which must be dissolved in the liquid in a close vessel by the assistance of a gentle heat.

For the albuminous mixtures, equal parts of chalk and red oxide of iron are rubbed down in a mortar, adding thereto eight times their united weight of a mixture of white of egg and water in equal proportions; if lime is substituted for chalk, only half the weight will be required. An equal weight of very finely powdered glass may also be substituted, to the extent of one-half of the weight of the oxide of iron. Instead of the diluted white of egg, an equal quantity of fresh uncoagulated blood may be employed for mixing with the lime, chalk, oxide of iron, and powdered glass, in the proportions given above.

Either of these varnishes or albuminous mixtures is poured into a shallow tin dish, of a suitable shape to admit a frame of matches, which is dipped into the same, so as to allow the fluid to cover completely the inflammable composition of each match, and slightly to adhere to the wood above.

The same varnish and albuminous mixtures may be used for rendering the scaleboard of the boxes in which matches are commonly packed, at least partially waterproof, and if an albuminous mixture be first laid on the boxes, then a coating of the shellac varnish to follow, the effect will be more complete. The application may be made with a brush, or in any convenient manner.

Safety Matches, ignited by rubbing against a prepared surface.—As serious accidents have sometimes been caused by the casual ignition of lucifer matches, a kind of match has been invented, which will not take fire, except when rubbed against a surface covered with a peculiar composition. A patent for matches of this description, the invention of J. E. Lundström, of Sweden, was taken out in this country in 1855 by Francis May. The matches are dipped in the usual way in sulphur, stearin, wax,

spermaceti, or any similar matters fit for communicating fire from the igniting compound to the wood or other material of the match.

The igniting compound applied to the tips of the match is composed of

6 parts by weight of chlorate of potash,
2 to 3 parts of sulphide of antimony,
1 part of glue weighed in the dry state.

The paste to be applied to the rubbing or friction surface is composed of

10 parts by weight of amorphous phosphorus,
8 „ of oxide of manganese or sulphide of antimony,
3 to 6 parts of glue weighed dry.

The ingredients must be thoroughly mixed, and care must be taken not to mix the chlorate of potash in the dry state with any of the other ingredients; it should be mixed first with the glue dissolved in warm water. The composition for the rubber may be spread with a brush or spatula on the side of the box which holds the matches, or on any other suitable surface.

These are the matches already alluded to (p. 139), as manufactured by Coignet & Co., of Paris: they are sold all over France under the name *allumettes hygiéniques de sûreté*, and have been ordered by the Minister of War to be used throughout the army. There is another modification of the same principle proposed by MM. Bombes-Devilliers and Dalemagne, in which the amorphous phosphorus is placed at one end of the match, and the chlorate of potash at the other, and the match being broken in halves, the two prepared ends are rubbed together; but this plan does not appear to have been adopted commercially. The Lundström principle has been adopted in Belgium and Germany, but owing to imperfect execution it has generally failed. When carefully executed, it is so all-sufficient, and in many respects so superior to the ordinary phosphorus matches, that it is only the prejudice entertained by the great mass of consumers, in favour of a match which will ignite anywhere by friction, that prevents its extensive adoption.*

MATCHES WITHOUT PHOSPHORUS.

To obviate all danger of poisoning, both to those who prepare the matches and to those who use them, it has lately been pro-

* For the information contained in this paragraph we are indebted to Mr. Albright.

posed to make lucifers tipped with a composition containing no phosphorus whatever, either in the ordinary or in the amorphous state. This is so far a return to the earlier method of making chemical matches, which were originally tipped with a mixture of chlorate of potash and sulphide of antimony, the use of phosphorus being of later date.

H. Hochstätter, of Darmstadt, uses a paste of the following composition :—

Chlorate of potash	18 parts,	. . . . .	18 parts.
Chromate of potash	4 „	or chlorite of lead	3 „
Binoxide of lead	9 „	. . . . .	9 „
Sulphide of antimony	18 „	. . . . .	18 „
Gum	5 „	or wheat-starch .	6 „
Manganese . .	2 „	or pumice-stone .	2 „
Flower or milk of sulphur . . .	2 „	. . . . .	2 „

The ingredients are first mixed together, and afterwards the gum or starch dissolved in water is added, and the whole is to be finely ground, and stirred with a piece of wood or metal.

G. Canouil (patent 1857, No. 2817), also prepares matches without phosphorus. The three following compounds are for dipping matches to take fire by rubbing over any suitable smooth hard surface, such as window-panes, looking-glasses, varnished or other wood, paper, board, &c.

No. 1.

Chlorate of potash	75 parts,
Binoxide of lead	35 „
Iron pyrites	35 „
Gum, dextrin, or glue . . .	10 „

No. 2.		No. 3.	
Subsulphocyanide of lead	3	Chlorate of potash . .	3
Chlorate of potash . .	10	Bichromate of potash .	2
Bichromate of potash .	2	Pulverized glass, pumice-stone, &c.	3
Gum, dextrin, or glue .	2	Gum, dextrin, or glue .	2

The following mixture (No. 4) is for matches intended to ignite either by rubbing over a surface provided with a suitable quantity of the same mixture, or better with the mixture No. 5 :

No. 4, for matches.

Chlorate of potash	1 part,
Nitrate of lead	1 „
Bichromate of potash	2 parts,
Pulverized glass, sand, pumice-stone, &c.	4 „
Gum, dextrin, or glue	6 „

No. 5, for rubbers.

Clinkers reduced to very fine powder	1 part,
Fine emery powder, sand, pounded glass, pumice-stone, &c.	1 „
Chlorate of potash	6 „
Minium	1 „

Payen, in his "Chimie Industrielle," (4me ed. 1859, tome ii. p. 564,) gives also the following formulæ, as due to M. Canouil:

1.—Paste for matches to be ignited by friction on the ordinary rubbers of pounded glass, or fine sand, and stiff glue.

Chlorate of potash	5	6	5
Oxysulphide of antimony	0·5	0·5	3
Peroxide of lead	3	or sulphur or cyanide of lead	2
		or glass bichromate of potash	2
Gum	2	2	2
Water	8	8	8
	18·5	18·5	20

The following also yields good results:—

Chlorate of potash	28·5	Glass pounded and sifted	10·8
Stiff glue	5·4	Sulphur ditto	85·0
Bichromate of potash	2·9		
Nitrate of lead	2·7		135·3

The following require a particular rubber:—

Paste for matches.		*Paste for rubber.*	
Chlorate of potash	7·3	Chlorate of potash	6
Nitrate of lead	2·3	Iron dross	1
Bichromate of potash	2·3	Emery	1
Sulphur	1·3	Red lead	1
Gum arabic	6·3	Stiff glue in quantity sufficient to make the paste adhere to wood, card-board, or metal.	
Water	18·0		

Another paste serves to tip matches which ignite by friction on a surface coated with the same paste, with the addition of $\frac{1}{5}$ of its

own weight of finely pounded emery or iron dross, and a sufficiently adhesive solution of glue:—

Chlorate of potash	5
Bichromate of potash	2
Glass in impalpable powder	5
Pounded gum	15
Water	6

The first three substances must be triturated together on glass with a glass pestle and then mixed with gum, previously diffused through the quantity of water above indicated.

Lastly, the same paste, with the addition of 0·8 of golden sulphide of antimony will render matches very easily inflammable by friction on any rough surface, or even on a polished surface.

In connection with these non-phosphoretted matches, we may notice a composition for *trains* or *safety*-fusees invented by Messrs. Gurney and Mills, and patented in 1857. It is prepared as follows:—

"Take equal parts of chlorate of potash in fine powder and ferrocyanide of lead (which latter is formed by precipitating a solution of nitrate of lead with an equivalent quantity of solution of ferrocyanide of potash). Ferrocyanide of tin or zinc, &c., might be used in place of lead, although lead is preferable. These two substances in about equal proportions we mix with alcohol to the consistence of a paint, and apply with a camel's hair pencil or any similar device to a strip of paper or equivalent material, which is to be encased in a winding of fibrous material, tape, or similar substance, that will keep the powder in its place when dry; and we prefer that the winding should be coated with shellac or other varnish to resist moisture, although the train or fuse thus formed will explode when slightly damp, and will not be injured in its explosive qualities by being wetted, if it be dried before using. The fusee formed of the aforesaid composition, enclosed in a strip of paper, or winding of fibrous material, may be rendered waterproof by immersion in tar, pitch, gutta percha, or equivalent material. The line painted or formed of this compound need not be over $\frac{1}{10}$ of an inch in width, and about two grains to the foot will be found sufficient. The safety train or fusee thus formed will be found to be exceedingly rapid in its ignition and cheap in its manufacture; can be used for giving signals to great distances by night or by day; as a substitute for electricity for blasting; for cannons and mortars; for setting-off

fireworks, and for a great variety of other purposes. The powder formed as above specified might be used in place of gunpowder or other explosive compounds, although specially adapted to the manufacture of trains or fusees, and will not detonate except between hard surfaces and under a very heavy blow; and we have found practically that fusees or trains thus made will not fire loose gunpowder, on account of the rapidity of the explosion scattering the powder; hence its safety under many circumstances; but when the gunpowder is the least confined, it explodes."

Machinery for Cutting and Dipping the Matches.

A great number of machines have been invented for cutting wood into splints for matches, some of the most important of which we shall describe, observing, however, that the cutting is seldom performed in the same establishments as the subsequent operations.

The dipping is mostly performed by hand in the manner already described, at least in this country. Machines have, however, been invented for arranging the splints in the frames, and dipping them into the paste; some of these will also be described.

A form of machine much in use for cutting square splints is that of which an improved form has been recently patented by F. Tillett (1859, March 23rd, No. 746). In this machine a set of reciprocating lancers or cutters, for grooving the block to be cut into splints, is combined with a knife or cutter for slicing off the grooved portions, in such manner that the cut of the slicing knife shall take place at right angles, or nearly so, to the cut of the grooving instruments. "The block to be cut may either remain at rest during the operation, in which case the slicing knife must have imparted to it a reciprocating motion (at or nearly at right angles to that of the grooving cutters), or the said knife may remain at rest and the grooved block be moved up past it. The cutting edges of both the knife and the grooving cutters may either be at right angles or inclined to the directions in which they respectively move. I prefer causing the grooving cutters to move horizontally and the slicing knife vertically, but this arrangement may be modified as desired."

"Fig. 30 is a side elevation; Fig. 31 is a plan; and Fig. 32 is a vertical section, through the line *a b* (Fig. 30) of the machine. A is the frame, which is bolted or screwed firmly to a bed plate or floor; B is a bracket bolted to the frame A, which carries a

guide C; D is a screw, supported in bearings formed on each end of the guide C. One end of this screw carries a ratchet wheel E, into the teeth of which a rod F, acting as a pawl, takes. This pawl is connected through a band G to an eccentric H on

FIG. 30.

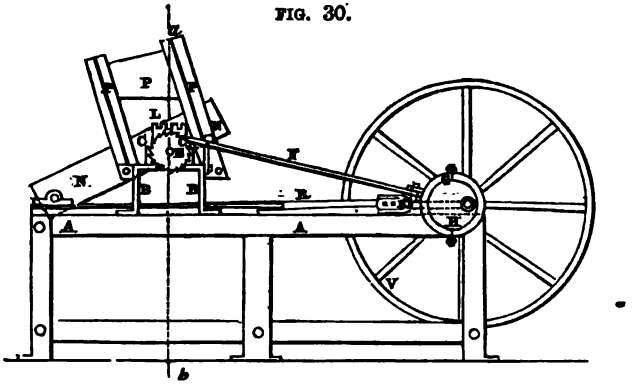
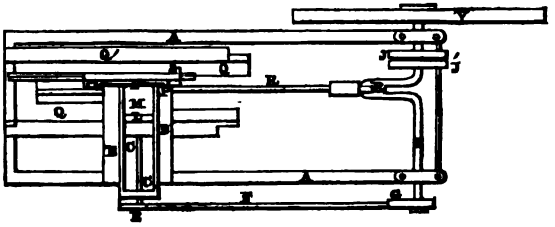
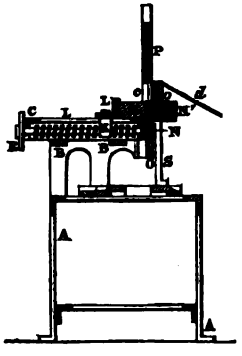


FIG. 31.



a shaft I, to which shaft rotatory motion is communicated through a pulley J J; K is a threaded nut working along the screw D, and to this nut a metal block L is screwed or bolted; L′ is a slot formed in the guide C, through which the bolt connecting the block to the nut travels; M is a block of wood from which the splints are to be cut; N is the lance carrier, set at an incline, as shown at Fig. 30; and N′ are the lances, inserted in a box which is placed in an aperture formed through the lance-carrier, and there held by a screw or screws. The carrier N is free to slide in V-grooves formed in guides O O′, and has a reciprocating horizontal or nearly horizontal motion imparted to it, as will be hereafter explained; P is a guillotine knife

FIG. 32.



or cutter, which travels in grooves formed in the guides P′ P′, and which works at right angles or nearly so to the lances N′; Q is a frame which works in V-grooves formed in a guide Q′, secured to the frame A. A horizontal reciprocating motion is imparted to this frame Q through a shaft R, connected to it by a link at one end, which shaft carries a crank R′, connected to the shaft I, and to which rotatory motion is imparted through the pulley J; S is a bracket to connect the carrier N to the frame Q; *c* is a steel plate fitted to the guide O, between which and the knife the splints pass; V is a fly wheel to regulate the motion of the whole machine. There are three distinct motions in the machine; first, that which causes the wood to advance to the knife; second, the reciprocating motion of the lance-carrier; and third, the vertical motion of the knife.

"To place a block of wood on the guide C, the pawl is removed from the teeth in the ratchet wheel, and allowed to rest on a bracket T (Fig. 30) formed for that purpose; the ratchet wheel is turned by hand in the reverse direction to that in which the pawl pushes it, whereby the nut K is driven backwards along the screw D, taking with it the block L until the block is brought far enough back to allow of the wood M being placed on the guide C. The pawl F is then thrown into gear, and at every revolution of the shaft I moves the ratchet wheel in the direction of the arrow one tooth, which causes the wood to advance far enough for the guillotine knife at each stroke to slice off the thickness of a splint. As the shaft I revolves, it communicates a reciprocating motion to the frame Q, which imparts a similar movement to the lance-carrier N, the lances in which, as the carrier passes the wood M, lance or cut it with as many cuts as there are lances in a horizontal direction; as soon as they have passed the wood, the knife P descends, and the wood falls in splints for matches between the knife P and the steel plate *c* on to a receiver *d*.

"An apparatus not shown in the figures is fitted for holding down and steadying the wood, the pressure on which is regulated by springs and screws or otherwise."

Another form of machine, applicable to the formation of either square or round splints, consists of a perforated metal plate, through which the block of wood is made to pass by pressure, the perforations in the plate being so shaped and arranged as to cause the block of wood, when pressed against its face, to be

divided or split into a multitude of small rods or splints, and these splints protruded through the perforations in regular-formed rods. Such a machine was patented by Reuben Partridge in 1842 (No. 9295). Fig. 33 represents the face of one of these plates, having a multitude of circular holes pierced through it; Fig. 34 is a section

FIG. 33.

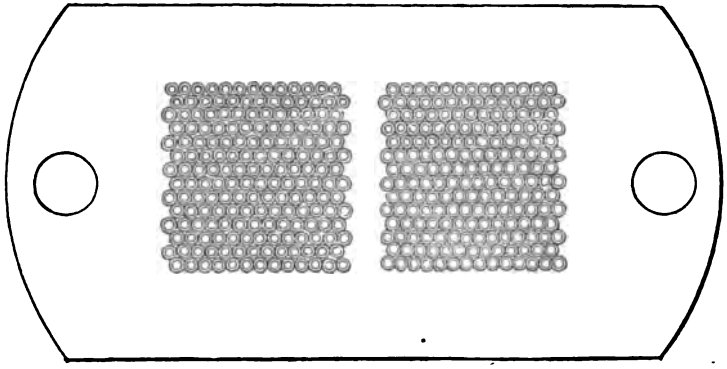
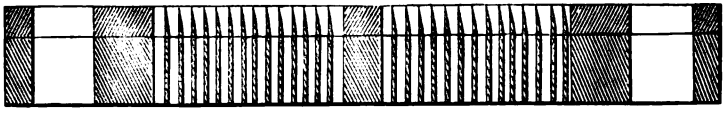


FIG. 34.



of the same taken through the plate in the direction of a right angle to the face. The forms of the perforations are cylindrical throughout, except at their openings on the face, where they are slightly countersunk for the purpose of presenting sharp cutting edges to the wood when pressed upon it, and in order to afford more easy entrance. The size of the perforations in the plate must depend upon that of the required splints or matches to be produced; but it is to be observed that they must be as close together as possible, allowing sufficient substance of metal to afford strength and resistance to the pressure when the wood is forced through. And the reason why the apertures must be so closely contiguous is that there may be as small a space of surface or blank between the holes as possible, in order that resistance to the passage of the wood may be avoided, and that, indeed, the whole area of the block of wood may be compressed laterally into the countersunk openings and forced through the cylindrical perforations. Though it is intended generally to split the wood and form the splints into cylindrical rods, the perforations in the

plate may be made of any other figure, and thereby enable splints of other forms to be produced by forcing wood through them. The plate has a steel face, strengthened by a bell-metal back, and is about three inches wide by six inches long, and nearly an inch thick. This plate may be employed in connection with any suitable pressing apparatus. The mode which has been found to answer is to fix the back of the plate against a firm resting block or bearing, having an aperture equal to the area of the perforations in the plate, and then place the end of the piece or pieces of wood in the direction of the grain against the face of the plate within the area of the perforated parts. A plunger, or a lever, or any other suitable mechanical agent, being then applied to the back or reversed end of the piece of wood, it may be forced through the perforations in the plate, being first split as it advances by the cutting edges of the holes, and afterwards compressed and driven through the perforations in the plate, coming out on the opposite side or back of the plate in the form of a multitude of distinct splints, according to the shapes and dimensions of the perforations.

We shall next notice the invention of Edward Zulzer, of New York (patented in England in the name of J. H. Johnson, 1854, No. 418), which "relates to the manufacture of that class of matches known as 'vestas,' and also to the production of the ordinary wooden matches, and consists in the employment of a drum if wax matches are to be manufactured, round which drum the wax wicks are wound. These wicks are then passed along between grooved feeding rollers and corresponding guide grooves in fixed tables, until their ends enter suitable holes in a moveable dipping-board, whereupon, by means of knives worked by the machine, they are cut into proper lengths, and thus made ready for dipping into the combustible preparation. The dipping-board is perforated with a large number of holes arranged in vertical and horizontal lines, and each horizontal line is filled at one revolution of the driving shaft. As many wicks are wound over the drum as there are holes in a horizontal line, and after each horizontal line has been filled, the dipping-board is raised to bring another line in front of the grooves in the tables. In this way the operation continues until the dipping-board is completely filled, when it is removed and a fresh board substituted.

"By a slight modification of this mechanism, and a simple arrangement of saws and guides, the machine may be made to

manufacture wooden matches, which are passed between the feed rollers and into the dipping-board, in the manner before described.

"Fig. 35 represents a side elevation of one modification of the machine. Fig. 36 is a longitudinal vertical section of the same. Fig. 37 is a plan of the machine. Fig. 38 is a front elevation of the dipping-board detached; and Fig. 39 is a corresponding side view of the same filled with matches ready for the dipping process. A A are the side frames or standards of the machine, carrying the large drum B, working in the bearings C C. Round this drum are wound the wax wicks, marked with dotted lines in the figure, to be cut into suitable lengths for matches, each wick being passed along the guide-grooves D in the fixed table E, thence between the pair of grooved feeding rollers F, and finally through the first guide-board G. The feeding rollers are driven from the main driving shaft H, which is fitted with a fly wheel and winch handle I. On the opposite end of this shaft is keyed the segmental wheel J, which gears with the spur pinion K fast on the end of the shaft carrying the lower feeding roller. This pinion gears with a corresponding pinion L on the upper feeding roller, whereby an equal speed is imparted to both rollers in contrary directions. M is a carrier wheel, which receives its motion from the pinion K, and gears with the large spur-wheel N on the end of the drum shaft O. A pair of shears or cutters P P^1, are situated at the edge of the guide board G. The lower or moveable portion P^1 of the shears or cutters is fitted with a pair of horizontally slotted brackets Q, the slots of which fit over the crank pins R in the driving shaft. The lower end of each bracket is attached to a short vibrating lever S, fast on the rocking shaft T, which is supported in bearings in the framing of the machine. A transverse spindle or rod U connects the two free ends of the levers S, and to this rod are attached the palls V, which take into the racks W on each side of the vertical sliding frame X. This frame serves to carry and elevate the dipping-board Y, and slides in the vertical grooves Z formed in the inside of the standards A A. It will thus be obvious that each time the brackets Q descend, the free ends of the levers S will rise and carry with them the palls V, which will move upwards, the frame carrying the dipping-board to the extent of one tooth, thereby bringing another horizontal row of holes in correspondence with the holes or grooves in the second guide board *a*. The frame X, which carries the

dipping-board, is fitted at the back with a second pair of racks *b*, and is held in its position when elevated by the fixed detents *c*

FIG. 35.

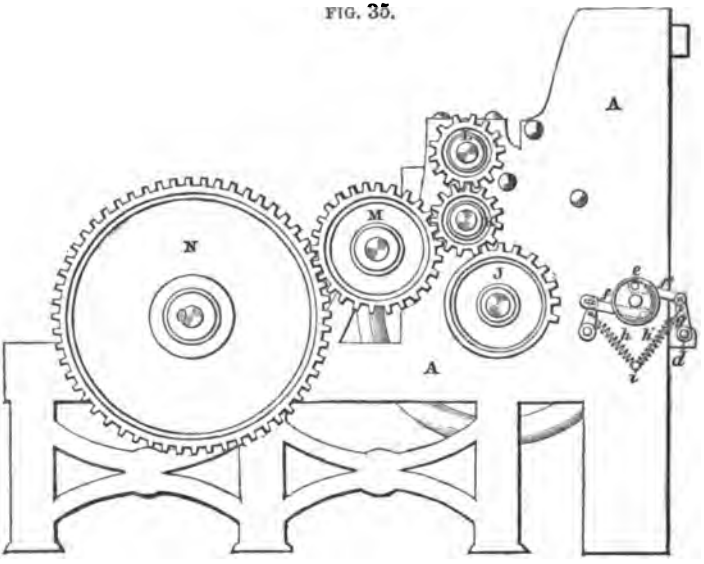
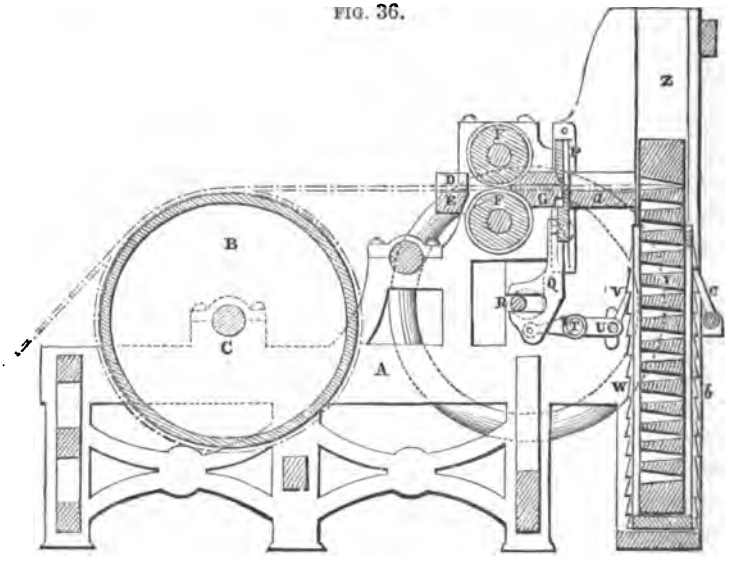


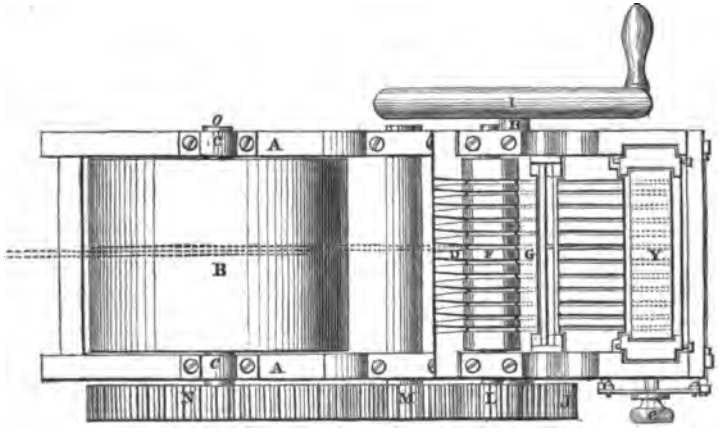
FIG. 36.



on the transverse rod *d*. *e* is a small button or knob which is capable of being turned slightly; it is carried by one of the stan-

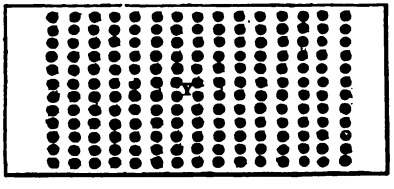
dards A, and connected by means of the two short links *f f'*, and cranks *g g'*, to the respective transverse rods *u* and *d*. This arrangement is for the purpose of effecting the simultaneous releasing of the palls V and detents *c* from their respective racks

FIG. 37.



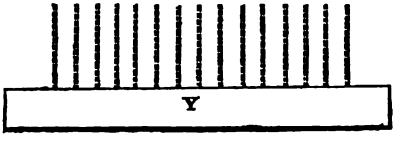
when the dipping-board has been filled and requires removing. The palls and detents are held in contact with their racks by the two helical springs *h h'*, connected with the cranks *g g'* and secured at their opposite extremities to the fixed stud pin *i*.

FIG. 38.



"Previous to starting the machine, as many wicks are wound one or more times round the drum B as there are holes in a horizontal row in the dipping-board Y. One end of each wick is then inserted into its corresponding groove in the guide board E, and is then passed between the corresponding grooved rollers F F, and finally through the holes in the fixed table G, their ends being left just clear of the cutters P P. The machine is then set in motion by turning the winch handle I, which causes the segmental wheel J fast on the end of the driving shaft H to revolve, and by its revolution to drive the pinions K and L,

FIG. 39.



which actuate the feeding rollers F F. As there are fewer teeth in the segmental wheel than there are in the pinions K, it follows that these pinions, with their respective rollers, will only make a partial revolution, and then stop, for every turn of the segment wheel. This partial revolution is just sufficient to draw off such a length of wick from the drum B as is required to form a match; but this length may of course be varied, by using segmental wheels with a greater or less number of teeth in them. By the motion of the feeding rollers before described, the ends of the wicks are pushed forward in the grooves of the second table *a*, and inserted into the top row of the conical holes in the dipping-board Y, as shown in the figure. By this time, the lower or moveable cutting blade P^1, which has been hitherto below or out of the way of the wicks, begins to rise by the action of the crank pins R, and as it ascends it cuts off or severs a suitable length of wick from the whole of the wicks simultaneously, thus leaving the top horizontal rows of holes in the dipping-board filled with suitable lengths of wick ready for being dipped, as shown in the detail, Fig. 39. The continuous movement of the driving shaft now causes the blade P' to descend, and in its descent the palls V are elevated in the manner before described, thereby raising the frame X, and with it the dipping-board Y, to a sufficient extent to bring the next consecutive horizontal row of holes in correspondence with the grooves in the table *a*. The board is retained in its elevated position by the detents C during the time of filling the consecutive rows of holes. When all the rows are filled in the dipping-board, the palls and detents are released by turning the knob *e*, when the frame X drops, and the board Y is removed to make room for another. It will thus be obvious that for every revolution of the main driving shaft a row of holes will be filled; and when the board is entirely full, it is taken with its lengths of wick to the dipping vessels, when the matches are completed by being dipped into the phosphorescent compound.

"I may here observe, that I do not confine myself to the making of wax tapers or matches alone, as by a very simple arrangement of saws and guides, suitable strips of wood may be introduced between the rollers F F, and passed through into the dipping board Y. The strips of wood are cut and delivered in a manner substantially the same as that before described in reference to wax tapers.

"Other suitable materials as well as wood may be used for the manufacture of matches by this machine. In the full-sized machines, each horizontal row of holes in the dipping-board will contain as many matches as will fill an ordinary sized box, and consequently at each revolution of the driving shaft a number equivalent to a box of matches will be inserted into the board. By a machine of this description one person may prepare as many as 50,000 boxes of matches per day."

Messrs. G. Bell and G. C. Grimes have taken out a patent (1856, No. 1275), for certain improvements in the manufacture of frictional matches and fusees, as follows: "In making frictional matches, in place of the pieces of wood of which they are composed being of equal thickness at the ends as at the other parts, they are made pointed, by which they can be dipped into the stearine and into the igniting compound in bundles, in place of their being held in frames, and they are cut by machinery in the following manner:—A blade is arranged to produce a parallel shaving or thickness of wood, as heretofore, and there are combined in the same machine two inclined blades, so that the edges of the shavings or pieces of wood are bevelled off, and the wood for each match is pointed at one end; hence, when held in bundles or quantities, they may be dipped in the materials used for making frictional matches. In place of dipping frictional matches in sulphur, we sometimes dip them in resin or pitch. In making fusees, in place of the simple prepared paper, heretofore used, a shaving or thin cutting of wood is placed on one side of the paper to give strength thereto, and by extending beyond the paper the wood becomes a handle to hold a fusee when using it.

"Figure 40 shows a longitudinal section, and Figure 41 a plan, of a machine suitably arranged for cutting matches with angularor pointed ends. a is the cutter block, which is furnished with vertical and horizontal cutters of the ordinary kind, and is moved to and fro on guides a^1 a^1 by means of the connecting rod a^2 attached to the crank axis a^3, which receives motion by a strap from a steam engine or other motive power. The blocks or pieces of wood to be cut are fed into the box or holder b, which is supported above the cutters by arms affixed to the framing of the machine. c is a lever arm to

support the block of wood in the holder whilst the cutters *d d* are acted on, to cut off an angular shaving from each end of the piece of wood to be cut, so as to bevel it off, as shown in Fig. 42. The cutters *d d* act at right angles to the cutters *a a* in the

FIG. 40.

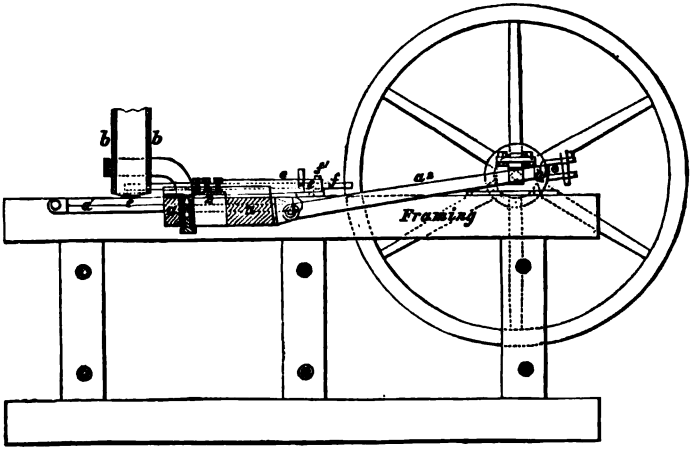
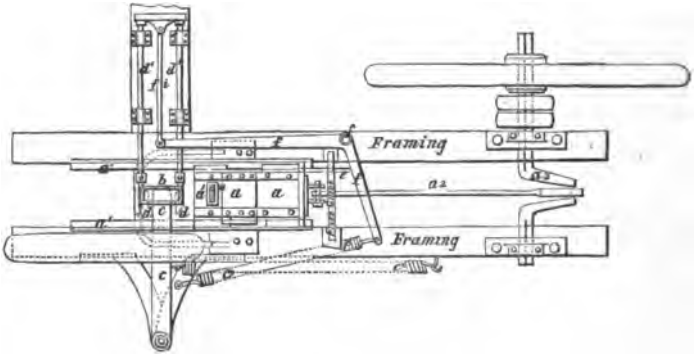


FIG. 41.



following manner: *e* is an arm fixed to the cutter block *a*; the arm *e*, in the backward movement of the cutter block *a*, acts against the lever arm *f*, moving on the fulcrum f^1, fixed to the framing of the machine; the other end of the lever *f* is connected by a pin joint to the link f^2, which is connected by a cross head to the slide rods d^1 d^1, to the other ends of which the cutters *d*

d are fixed, there being sockets with set screws on the ends of the rods d^1 d^1, into which the ends of the cutters d enter, and

FIG. 42.

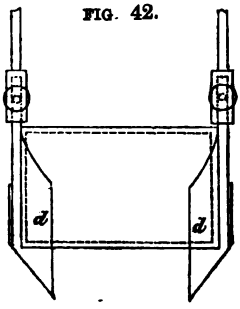


FIG. 43.

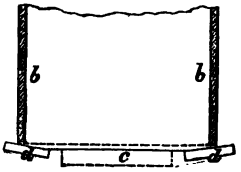
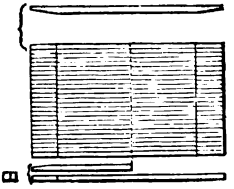
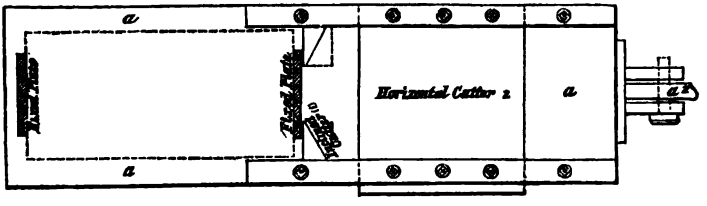


FIG. 44.



are capable of being adjusted and fixed at a proper angle for forming points to the matches when cut. The levers c and f are drawn back after being acted upon by springs c^+ f^+ as shown. The cutters d d, having bevelled off the edges of the piece of wood, the cutter block a in coming forward pushes the lever c from under the piece of wood to be cut in the holder, which will then rest upon the cutter block a; and the vertical cutters (1) will first score the under surface of the wood, and then the horizontal cutter (2) will take off a slice or shaving, which falls through the opening in the cutter block, cut into matches having pointed or bevelled ends, which are afterwards cut across their length; and the pointed ends may then be dipped, when held in bundles, in the materials used for making frictional matches

FIG. 45.



"Fig. 45 shows a plan of another arrangement of cutter block a, suitable for cutting matches with pointed ends. The cutter block a in this arrangement of the cutters is sufficiently long to support the piece of wood in the box or holder when the cutters have moved back to their furthest position. 1 1 are cutters, which are placed at an angle in front of the horizontal cutter 2,

so that as the cutter block moves forward, the cutters 1 1 first bevel off the edges of the wood, and the cutter 2 then takes off a shaving having bevelled edges. A number of these shavings are then packed edgeways in the box or holder, and are again cut by the same cutters into matches which will have points bevelled off on two sides. Fig 46 exhibits a series of shavings packed edgeways to be be cut into matches with pointed ends, also side and end views of these matches; and Fig. 47 is a plan and edge view of a shaving formed by the cutters 1, 2.

FIG. 46.

FIG. 47.

"Fig. 48 shows an edge and side view of fusees made according to our invention. *a* is a shaving or thin cutting of wood on which the prepared paper *b* is fixed or cemented. This thin shaving is employed to give strength to the prepared paper, and to form a handle to hold the fusee by when using it."

FIG. 48.

The following patents relate to machinery which, besides cutting the splints, performs the dipping and other operations connected with the manufacture:

Louis Urion has invented machinery (patented in this country in 1856, No. 2594) for the manufacture of flat or square matches, and for shaping or cutting common boxes for enclosing such matches. The manufacture, which is performed mechanically, consists—1st, in the cutting up of the wood; 2ndly, in the arrangement and disposition of the cut matches in parcels suitable for sulphuration; 3rdly, in the mechanical application of the phosphorus; 4thly, in the drying of the matches; 5thly, in the shaping or cutting of wood suitable for making common boxes; and, 6thly, in the stamping and marking or printing the match boxes. The machinery is represented in the annexed diagrams, in which the same numerals represent the same parts in all the figures where they recur.

Fig. 49 is an elevation of the whole of the machine, showing also the means of transmitting the movements; Fig. 50 is a plan of the same machine; Fig, 51 is a longitudinal vertical section, in

FIG. 49.

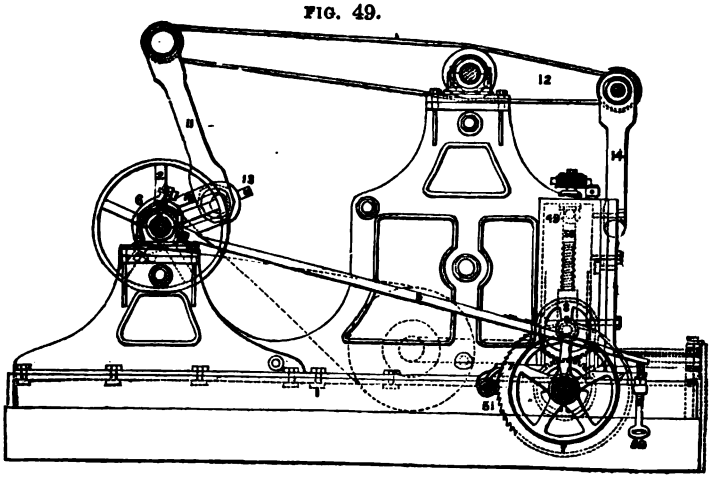


FIG. 50.

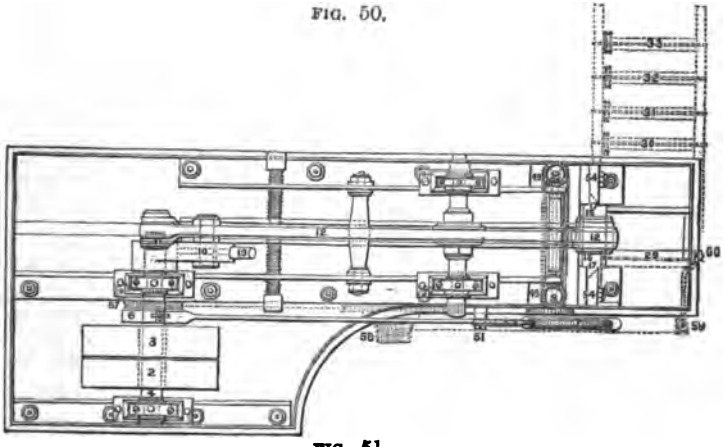
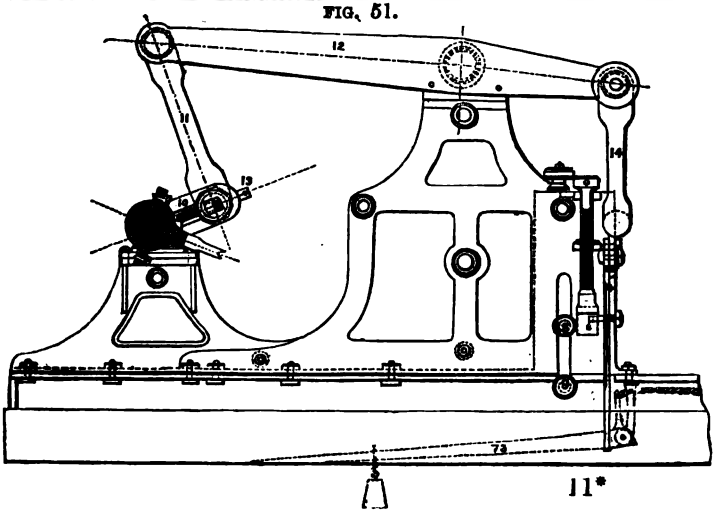


FIG. 51.



a plane parallel to Fig. 49; Fig. 52 is an end view of the machine; Fig. 53 is an elevation of the printing press or apparatus which stamps the boxes; Fig. 54 is a front view of Fig. 53; and Fig. 55 is a separate view of the ink-box or reservoir; Fig. 56 is the elevation of the mechanism which separates the cut matches, so as to sulphur and phosphorate them in quantities; Fig. 57 is the front view of this same machine; Fig. 58 is a plan of the same; Fig. 59 is the arrangement of a parcel of matches ready to be sulphurated and phosphorated; Figs. 60 and 61 are plans of Fig. 59; Fig. 62, front, back, and edge view of a knife for the manufacture of the match boxes; Fig. 63, front view, edge or side view, and back view of a knife for cutting the wood into short pieces for the manufacture of square matches; Fig. 64, front edge and back view of a knife for cutting the square matches; Fig. 65, front view, side view, and back view of a knife and knife-carrier or holder for the manufacture of flat matches; Fig. 66, also a knife for flat matches; Figs. 67, 68, 69, elevation, plan, and section of the part serving to remove from the knife the thin wood or scaleboard which is to form the sides of the boxes: Fig. 70, vertical section of the sieve saw or cutting bit, for the manufacture of round boxes; Fig. 71, the plan of the iron frame in which to place a block of flat matches; Figs. 72 and 73, plan and elevation of a block of wood serving to push the piece of wood being cut, the use of which will be explained; Figs. 74, 75, 76, plan, elevation, and end view of the separate cutter of the flat matches; Figs. 77, 78, 79, plan, elevation, and end view of the screw frame serving for the manufacture of the flat matches in block.

1, foundation plate; 2 and 3, fast and loose pulleys; these two pulleys are mounted on the axis 4, to which they transmit a rotatory motion which they receive from any suitable motive power. 5, rod of eccentric 6; this rod, by means of its to-and-fro motion actuates the ratchet wheel 7, and turns the two spur wheels fixed on the shafts of the grooved cylinders 8 and 9, between which the wood passes, and by which it is advanced for the manufacture of square or flat matches, and for cutting scaleboard or sheets of wood for the manufacture of the boxes. On one end of the shaft 4, about the middle of the machine, is a crank 10; it has a radial slot or groove to receive the crank pin connecting the crank with the rod 11, and by it with the beam 12; the said crank pin, and with it the rod 11, may be caused to approach or

FIG. 52.

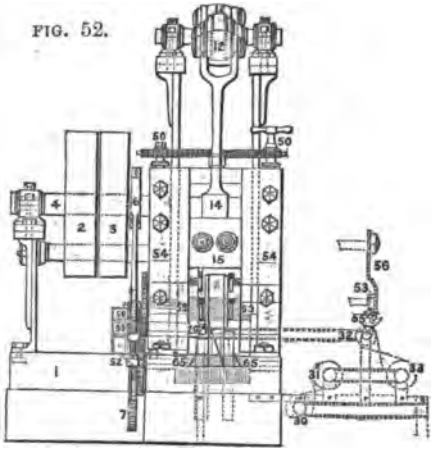


FIG. 53.

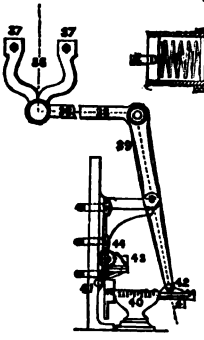


FIG. 55.

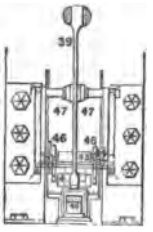


FIG. 54.

FIG. 56.

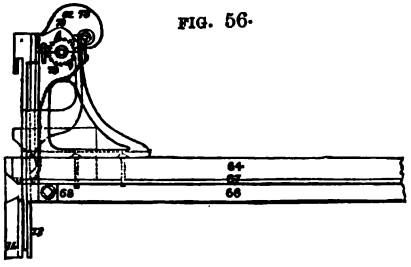


FIG. 57.

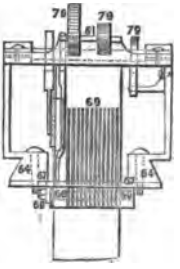


FIG. 58.

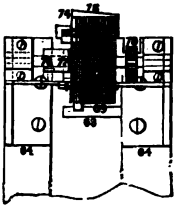


FIG. 59.

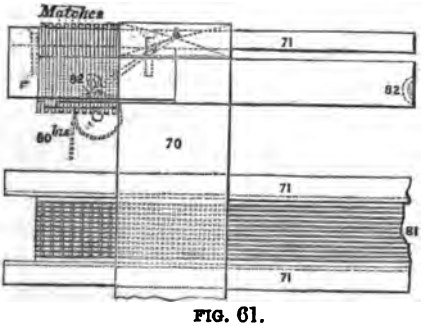


FIG. 61.

FIG. 60.

recede from the centre of the shaft 4, by means of a nut and screw 13 traversing the crank pin, thus increasing or reducing the throw of the crank. The beam 12 is moved by this connecting rod 10, and gives motion at its front part to rod 14, connected with the knife carrier; 15, frame supported and sliding in upright guides, and carrying the knife frame 16, and put in motion in slides 17 by rod 14. The knife frame is intended to receive four knives, operating one after the other, when required. The first knife 18 being fixed to the knife frame or carrier, serves to cut the wood into thin pieces, adapted for the manufacture of square matches. The second bevel knife 19, formed with rigid cutting grooves, serves to cut the square matches. The third knife 20 is intended for the manufacture of flat matches; it has two cutting edges, the lower one 21, and the upper one 22, so as to give a uniform thickness to the matches, to form which the wood is further vertically divided by the cutting teeth 23, 24, 25, 26, 27, and 28. The lower blade, which is fixed near the other, serves also to raise the matches which it has cut high enough to allow the knife to immediately act again; the matches fall on endless cloths mounted on the cylinders 29, 30, 31, 32, and 33. The fourth knife 34 is also for the manufacture of the flat matches; it is mounted on a frame, and provided with a piece 35, on which are fixed the blades which divide the wood in advance of the knife.

Printing.—36, bracket piece, with lugs fixed by two small bolts 37 on each side of the beam 12; at about the middle of its length the said piece puts in motion the horizontal rod 38, which gives motion to the lever 39 of printing press, which works at will. 40, support, with slides carrying the impressing part of the printing press. 41, impressing surface, having horizontal motion; it is furnished with type at its anterior part, and it is put in motion by the lever or beam 39, which pushes it backwards and forwards (the lower end being fitted between two brackets 42) as fast as the sheets are printed before being cut. 43, printing ink reservoir or supply box (shown in detail in Fig. 55), before which is a cylindrical pad or inking roller. 45, another cylindrical pad, carried by two springs 46, in front of the bearing frame, by means of a plate 47; this latter cylinder, in its motion up and down, passes in contact with the cylinder 44, placed before the ink reservoir, and thereby takes up a portion of ink over its whole surface, in order to ink the types, which it does in descending before the

FIG. 62.

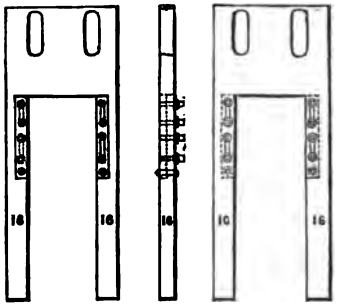


FIG. 63.

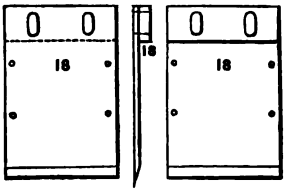


FIG. 64.

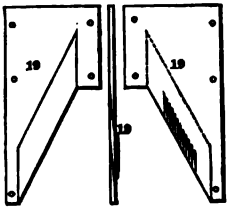


FIG. 65.

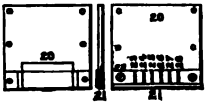


FIG. 66.

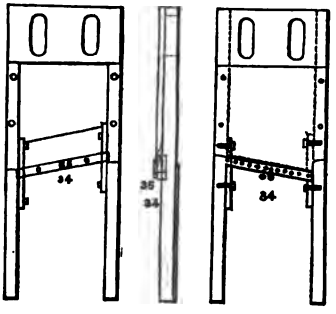


FIG. 67.

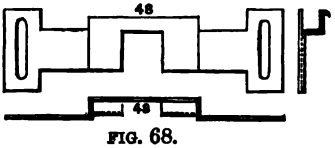


FIG. 69.

FIG. 68.

FIG. 70.

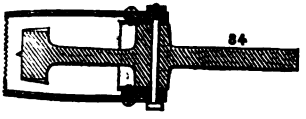


FIG. 74.

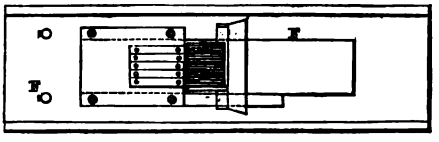


FIG. 72.

FIG. 71.

FIG. 73.

FIG. 75.

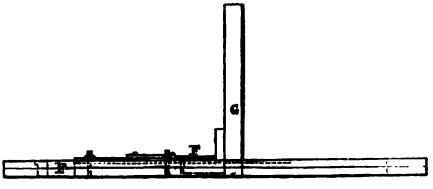
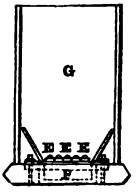


FIG. 76.



face of the type form or impresser 41. 48, bent plate, placed in front of the knife 18, which cuts the sheets for the boxes; it serves to prevent the sheets from rising with the knife, and at the same time for bringing them under the machine. 49, boxes on the right and on the left of the knife carrier, each containing a screw 50, for the purpose of lowering or raising the bearings carrying the toothed cylinders 8 and 9, which press the wood between them and bring it under the knife, the same movement raising or lowering the toothed gearing, the ratchet wheel 7 of which is prevented moving backwards by means of pall 51. 52, screw support for raising or lowering the rod 5 on the ratchet wheel 7, so as to make it take a greater or less number of teeth, as required for advancing the wood more or less between the two toothed cylinders above described.

The dotted lines indicate:—53, movement for effecting the sulphuring of the matches, the elevation of which is presented in front of the side plates; 54, endless cloths, traversing over the rollers 29, 30, 31; 32 and 33 serve as trays to carry the matches until perfectly dried; 55, cylinder with spatulas; it is put in motion by the ascending and descending of the rod 56, which gears in three small projecting teeth; this cylinder performs two thirds of its revolution by the motion of the rod 56, the other one-third of its revolution is performed by means of a counterbalance weight.

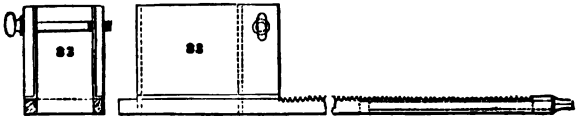
The spatulas just mentioned serve to supply the chemical composition to one of the upper faces of the flat matches before their elevation, and before their descent to the lower endless cloths; these cloths are put in motion by means of a pulley 57, mounted on axis 4, and the transmitting and turning pulleys 58, 59, and 60, and endless bands or straps conducted along the sides of the machine.

The square matches must be sulphurated and phosphorated each separately, although in quantities, in order to prevent their adhering or sticking together. This result is obtained by the mechanism 61, 62, and 63, the description of which is as follows: 64, tongues, sliding in the grooves or slots 65 of the plate 67, which is placed between them. On this plate are mounted and fixed the blades 69, by means of a heel-piece placed underneath, and fixed by screws and nuts 68. The blades 69 receive each row of matches which pass between them; the matches are moved

and maintained in position by a moveable cross bar 70, which engages in the rebates of the two parts 71. The whole mechanism has a to-and-fro motion towards and from the knife of the machine, which pushes it backwards; the anterior part 72 is inclined; the return towards the knife, in order to receive the matches, is performed by means of a lever 73, mounted on an axis, and carried by bearings under the foundation plate. In order to separate every row of matches to phosphorate them, two iron pieces 73ª and 74, independent of each other, although contiguous, move up and down by means of a gearing rod mounted in front of the frame of the knife carrier. This rod engages with a small ratchet wheel 76 and 77, raising or lowering the two parts above described, which elevate or lower each row of matches the required

FIG. 77.

FIG. 79. FIG. 78.



distance. As they advance, the two springs 78 and 79 serve, that on the right 79 to instantaneously lower one of the two parts after its escape from the tooth of the ratchet wheel, and that on the left 78 to raise the other part by the same means as the preceding. When the matches have reached the extremity of the blades 69, they enter other blades of wood 81, shown at 80 and 80 *bis*: when these latter blades, which have a length of about eighteen inches, are filled, they are secured at each end by bolts 82, and this enables the whole to be withdrawn in a mass for the purpose of sulphurating and phosphorating the matches. 83, iron frame, in which is placed a block intended to make flat matches. The wood, properly held, is cut up until on a level with the frame, and by this means matches in bundle are obtained which are neither to be sulphurated nor phosphorated. 84, augur bit or sieve saw, for making round boxes; the cover is made by the same means, but the bit is shorter. 85, wooden block, placed behind each block of matches, engaged in iron

frame 83; this block is destined to push the wood which is cut till entirely used up, and to prevent any loss.

Fig. 55 represents a longitudinal section of an ink box or reservoir. A, cylinder pierced with holes; B B, pressing discs closing the ends of the cylinder; C C, two spiral springs; D D, ends provided with pivots *d d*, and screwed into the cylinder; E E, covering of wool and buckskin surrounding the cylinder. The printing ink is placed inside the cylinder, and the whole being mounted as shown by the figure, it will be easily understood that if the springs are compressed, they constantly press against the discs B, and force the ink continually to be imbibed by the tissue or cloths surrounding it, and forming the ink surface.

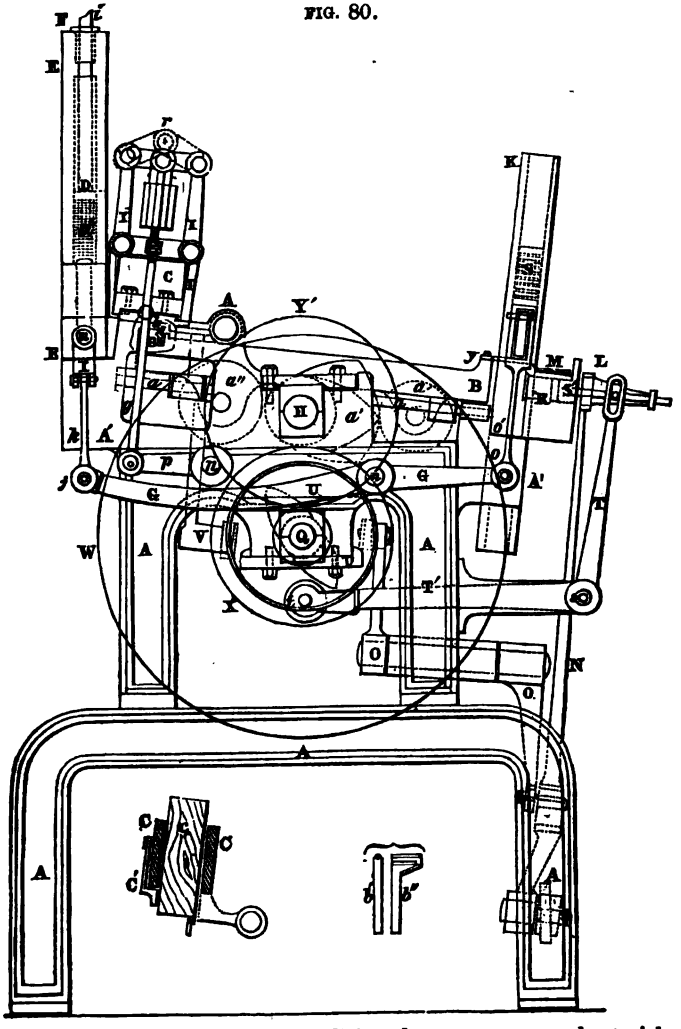
The flat matches for the use of smokers must, before being sent to the trade, be sufficiently separated from the block, so that they may be taken one after the other without any difficulty; this separation is effected by a partial cutting of the base of each match. This cutting is made by means of the apparatus represented at Figs. 74, 75, and 76, in plan, elevation, and end view. E, triangular bevel blades, having an edge somewhat narrower than the width of a match, and having between them a distance corresponding to the width which it is wished to have between the matches adhering to the block. These blades are fixed upon a plate secured to the frame. F, iron frame provided with slides. G, bearer or carriage on which is placed the block bundle of cut matches. The whole is mounted as shown in the three figures, and the bundle is pressed by the carriage against the knives which partially cut the base of every match. This accessory machine is fixed on the framework.

Thomas Cook's patent (1857, No. 2748) relates to improvements in machinery for cutting, framing, and packing wood matches. Fig. 80 is a side elevation of the machine; Fig. 81 is a front end elevation, showing especially the parts for cutting matches and filling frames; and Fig. 82 is a back end elevation, showing the parts for transferring matches from the frame to boxes.

"A A is the main framework, and A′ the upper portion of the same; B B, the sliding frame, with a steel blade at *y*, and working on guide rods *a*, and carrying the cutters *b*, being worked by the cam *a′*, working against the friction rollers *a″*; C, the guide box for the wood *c*, as at No. 1; and C′, stiff

springs; D, the match frame, having laths *d*, through the ends of which run the rods *e e*, and held together by spiral springs *g g* and *g' g'* are tightening or regulating nuts; E E, guides for the match frame to slide in; F, a cross bar, with a central stuffing box *h*, to cause friction on the rod *i*, which supports the

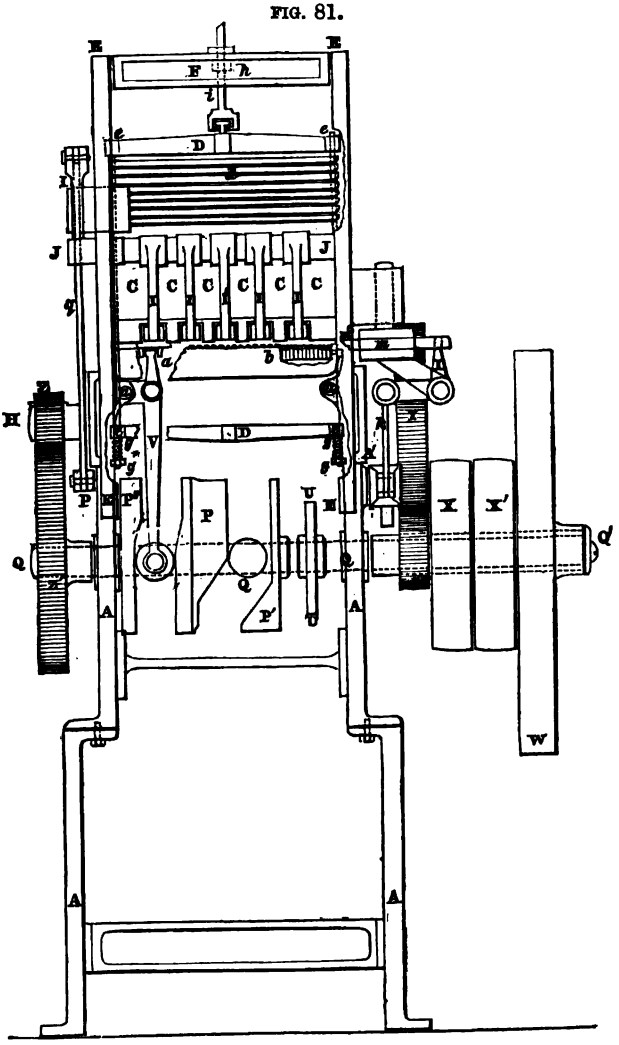
FIG. 80.



weight of the match frame D; G is a lever, connected at *j* by a short connecting rod *k*, with the bell crank *l*, for operating the slide *m*, wedge-shaped at the end *m'*, to insert between the laths;

the lever G is connected with the rocking shaft n, which has motion given to it by cams on the main shaft H, and the other end of G is connected at o with a vertical rod o', for working, by means of pauls x passing through slots in the guides of the filled

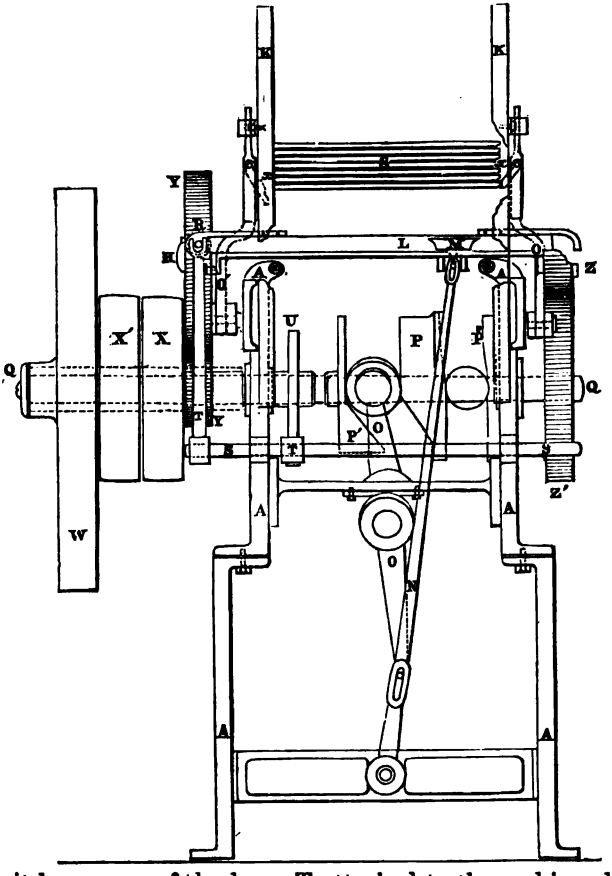
FIG. 81.



frame S working in the guides K while discharging; n' is another rocking shaft, with a lever p, working the connecting rod q, which operates the levers I of the feeding tongs I′ connected

to the shaft J; *r*, the toggle joints, and the dotted lines *r'*, show their motion, and, being connected to the levers I, open and shut the tongs I'. L is the trough receiving the matches, and has a block M which works in it from end to end by means of the lever N, worked by the lever or crank O, operated by the cams P P', on the cam shaft Q; R, the match cylinder; S', a plunger work-

FIG. 82.



ing in it by means of the lever T attached to the rocking shaft *s*, and worked by the lever T', also attached to *s*, and has at *t* a friction roller actuated by the cam U; the cams P P'', operate on the friction roller of the lever V, connected with the vertical box C at *u*, thereby giving it a transverse motion; W is the fly wheel; X X', two pulleys attached to a bush, so as to turn

loosely on the shaft; a pinion Y gears into the spur wheel Y' on the main shaft H, and on its other end is a pinion Z, gearing into the spur wheel Z' on the cam shaft Q. No. 2 is one of the steel cutters, full size; *b'* being a plan or back view, and *b''* a side view.

"It will thus be observed that machines made according to the said improvements consist of a main framework supporting a sliding frame carrying cutters *b*, Fig. 80, and No. 2, having above it a vertical box down which the wood is guided to the cutters, which in their backward motion cut the block, and in their forward motion carry the matches so cut into a frame D *d*, after which the box receives a slight transverse motion ready for the next cut, and so on alternately, the whole being operated by steam or other power. At the back of the main frame is an arrangement for receiving the frame holding the ready-dipped matches, and the action of the sliding frame before named forces the matches out into a trough, and thence into the boxes.

"The matches are cut from blocks of wood previously cut the length of the intended matches, and the box or frame in which they are placed is made their exact length, and wide enough to contain several, and they are prevented from falling through by stiff springs C', No. 1, pressing against the blocks. A series of feeding tongs work outside the box, passing through slots at the bottom, to grasp, force, and hold the blocks while being cut. A sliding frame underneath carries a series of single cutters, No. 2, placed the distance of the thickness of a match apart, and fitted into a conical or other groove in the sliding frame, so that one screw will hold a number in their place. In the match frame the laths are held together by rods having spiral or other springs, and are forced apart by a wedge or inclined plane *m'* at each end, and carried downwards the thickness of a lath at each stroke by the same means. The frame having the ends of the laths bevelled, they form an independent rack, and the frame slides in stationary grooves in front of the block frame or box C and the sliding cutter frame B. At the back of the machine are also stationary grooves to receive the match frames when discharging the matches by means of a thin steel blade *y* attached to the sliding frame for passing between each lath. A trough is here provided, and when filling round or other boxes, with a cylinder at each end the size of a match-box, with a slot in the side that is attached to the trough. On one end of the cylinders is a thin

rim on which to fit a match box, or it may be made with a bell mouth to fix it in. A plunger works in each cylinder from end to end, and a slide block fitted into the trough works similarly; and the ends of the slide are made to fit into the slots in the cylinders, so as to form a perfect cylinder; the several motions are produced by cams on the shafts. The main novelty in the improved cutters is, that they are formed and so arranged in their frame that on coming into contact with the wood blocks they cut out every alternate match, leaving the surface fluted where the matches have been ploughed out, and at the return stroke of the cutters, the block having meanwhile moved slightly transversely, the projections of the blocks are in their turn cut away and carried onwards towards the match-frame, and contiguity between the matches thereby prevented while in the dipping frame."

The very ingenious invention which remains to be described (patented by W. E. Newton, 1858, No. 1428, being a communication from a foreign inventor not named), relates to machinery for splitting or cutting the match-sticks in proper forms from the "bolt," or block, and the immersion of their ends in the sulphur and igniting compounds.

"The invention consists, first, in a cutting tool of peculiar construction, having circular and semicircular or convex and concave rollers, by which the match-sticks are cut smoothly and easily from the "bolt" or block, after which they are properly presented to an endless chain of clamps, by which they are conveyed to the sulphur and igniting compounds. Secondly, in an endless chain of clamps, constructed, arranged, and operated so as to effect the object above named, and also to allow of the discharge of the matches at the proper time and place. Thirdly, in a discharging device, arranged as hereafter described, for the purpose of discharging the finished matches from the clamps.

"In the accompanying diagrams, Fig. 83 is a side sectional elevation of the machine; Fig. 84 is an end sectional view of the same, taken in the line $x\,x$ of Fig. 83; Fig. 85 is an enlarged perspective section of one of the clamps and cams; Fig. 86 is a detached inverted plan of the cutting tool; Fig. 87 is a descriptive view, showing the manner in which the cutting tool acts upon the 'bolt' or block of wood; Fig. 88 is a plan view of a portion of the endless chain of clamps; Fig. 89 is also a plan view showing one method of operating the clamps.

"A is a platform or base, on which are placed four uprights *a*, which support a horizontal bed B; C is an endless chain of clamps

FIG. 83.

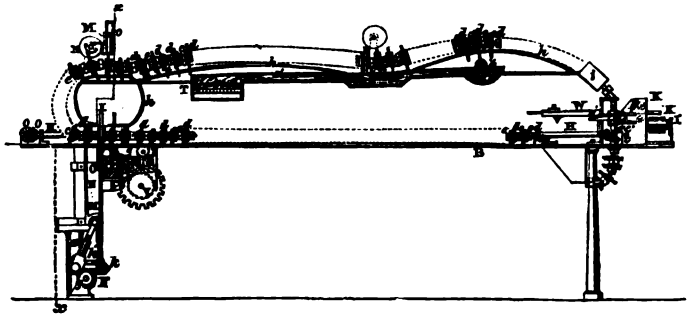


FIG. 84.

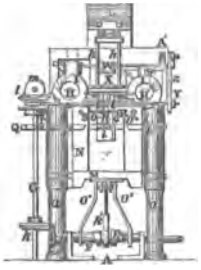
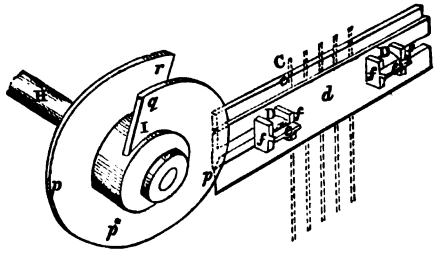


FIG. 85.



each of which is formed of wooden slabs *c d*, the ends of which are slotted longitudinally for a short distance, and are fitted on the links *e'* of chains D D, projections *f* being formed on the links, between which projections the clamps are fitted.

FIG. 86.

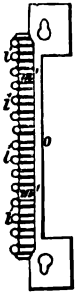


FIG. 87.

"The slab *c* of each clamp has a spring *e* bearing against it, the said spring having a tendency to press the slabs *c* against their fellow slabs *d*. The springs *e* may be formed of flat steel strips, having their ends slotted and fitted on the links *e'*. The construction of the chain will be understood by referring to Figs. 88 and 89, the former showing the peculiarity of the chain D D, the manner in which the clamps are fitted on them, &c., and the latter showing the relative position of several clamps, and a portion of the chains, the details of the latter not being shown. The construction of the chain may be modified in various ways, the important feature

being the clamps thereon. The endless chain of clamps C passes or works over guides *h* and through guide-boxes *i* (see Fig. 86).

"F is a shaft, which is fitted in suitable bearings on the platform or base A. This is the driving shaft of the machine, and to one end of it is attached a bevel pinion *j* (Fig. 84), gearing into a corresponding pinion *k* on the lower end of a vertical shaft G, which, by means of gearing *l* and a shaft *m*, gives motion to a shaft *n*, placed transversely on the front end of the bed B; the shaft *n*, by means of bevel gearing *o*, communicates motion to two shafts H H, which are placed longitudinally on the bed B, and extend nearly its own length. On each shaft H a cam I is placed. These cams are constructed precisely alike, and are formed of a section of a screw and two parallel portions, as will be clearly understood by referring to Fig. 85, in which the part included between the points *p p*, and marked *p**, is the screw portion, and the ends *q r* the parallel portions. The part *q* is of wedge or taper form, or it

FIG. 88.

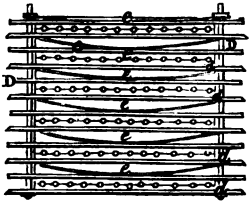
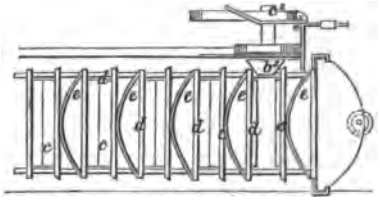


FIG. 89.



is made thicker than the screw portion, and at its junction with this portion is gradually tapered, the remaining portion having parallel sides. The cams I extend rather more than one revolution on the shafts H H, the ends *q r* projecting past each other. The cams I work between the slabs *c d* of the clamps, as will be hereafter more particularly referred to.

"To the back end of each shaft H a bevel pinion *s* is attached. These pinions gear into corresponding pinions *t t* on the lower sides of small upright shafts *u u* on the bed B. Each shaft *u* has a cam J on it, which are formed like the cams I, but work in a horizontal position (see Fig. 83), in which the screw part *a** of one of the cams J is shown clearly, as well as its parallel portions *b** *c**.

"K K (Fig. 83) are discharge rollers placed in front of the chain of clamps C, and on a line which passes between the two cams J J. An endless apron L is also placed transversely on the

bed B, directly in front of the rollers K; the use of this apron will be presently shown.

"M is a gate, which is fitted in a plate N, secured between the two front uprights *a a*. The gate M is fitted between proper guides in the plate N, and a reciprocating motion is given it from the shaft F by means of a crank *j'* and a connecting rod *k'*. In the upper part of the gate M is placed a cutting tool O, formed of a series of cutters *l'*, connected by semicircular cutters *m'* (see the inverted plan in Fig. 86). This cutting tool is, of course, constructed of steel. The position of the cutting tool, with the endless chain of clamps, is plainly shown in Fig. 83.

"The plate N is not rigidly attached to the uprights *a a*, but has a reciprocating lateral movement given it by a cam P on the shaft G. The cam P works within a loop Q, attached to one side of the plate N (see Fig. 84). The plate N has two horizontal rods *l''* attached to each side, and fitted and working in openings in the uprights, and serving as guides to the plate. To the upper part of plate N is attached a transverse bar R, having its front or face side grooved vertically, as shown at *l'''* and these grooves are placed in line with the circular cutters *l'* of the tool O (see Fig. 84), in which the circular cutters *l'*, or rather their position, is shown by dotted lines.

"In Fig. 84, S is a guide formed of a rod bent to form a horizontal top piece u^1, and having two vertical portions o^* o^*, which pass through the gate M.

"In Fig. 83, T represents the 'bolts' or blocks of wood from which the match-sticks are cut. The 'bolts' or blocks are sawed or got out of wood of proper thickness corresponding to the desired length of the sticks, which are cut from the bolt longitudinally with its fibre or grain. The bolts are placed one behind another on a bed U, and are fed to the cutting tool O by feed rollers V V, which may be worked in any proper way from the driving shaft of the machine. The lower edge of the bar R rests upon the upper surface of the front block T, near its front edge, as seen in Fig. 83.

"W is a discharge plate fitted in a guide X, so as to work in line with the 'bite' of the rollers K K. This plate is worked at the proper time from the shaft *n* by means of levers Y Y, the rod *z*, and a spring A' (see Fig. 84).

"M' is a hammer, which is placed above the chain of clamps C. This hammer is worked by a cam N' and a spiral spring O'. P' is a reservoir or basin in which sulphur is placed, and R' is a

basin in which the igniting compound is placed; S′ is a flue, which runs under both basins P′ R′; T′ is a furnace with which the flue is connected.

"The operation is as follows:—The bolts or blocks T are placed on the bed U, and motion is given to the shaft F in any proper manner. The gate M has a reciprocating motion given it by the crank *j*, and connecting rod *k*, and as the cutting tool O′ descends, the circular cutters *l*′ cut entire match sticks from the bolt, and form concave portions 5 (see Fig. 87), the semicircular cutters *m* forming convex portions 6. At the next stroke of the cutting tool it is shifted or moved laterally by the cam P, so that the circular cutters *l*′ will cut out the remaining half circle of the convex portions 6 which were formed at the previous stroke. The following or third stroke is the same as the first, the cutters *l*′ cutting out entire match sticks every alternate stroke, and in the intermediate strokes finishing or cutting out in match sticks the convex portions 6. The match sticks are retained in the cutters *l*′ during the upward movement of the tool O, and the sticks enter the clamp immediately above it; the grooves *l*‴ of the bar R, in connection with the guide S, keeping the match-sticks in line, and causing the sticks to be properly presented to the clamp; the guide S rising with the gate M until it strikes the under side of the bed B, and thus remaining until the gate has reached its culminating point. When the gate descends, the guide S descends with it a certain distance until the lower ends of the rods *o** *o** of the guide strike the base or platform A, when it remains stationary, so that the rod *k* will be at a point some distance below the upper edge of the bolt, and keep the sticks in line, so that they will enter the grooves *l*‴ of the bar R, the lower edge of which, in consequence of bearing on the end of the bolt T, prevents the same from being raised by the tool as the latter ascends. When the tool descends, the sticks are retained by the clamp, and a clamp composed of the wooden slabs *c d*, is fed over the cutter O, so as to receive the sticks cut by it at each stroke by means of the screw portion *p** *a** of the cams I I J J, the cams fitting between the ends of the slabs *c d*; the apron C therefore is moved intermittently, the movement being produced by the screw portions *p** *a** of the cams, and the 'dwells' being produced by the parallel portions *q r b** *c**, and the clamps are distended by the wedge-shaped parts of the portions *q b** of the cams, the springs *e* closing the clamps as the

parts q b^* leave them. The parts q of the cams I open the clamps to receive the match sticks, while the cams J open the clamps to allow the sticks to be discharged therefrom by the plate W, which is actuated as the clamps are opened by said cams, the plate W forcing the sticks between the rollers K K, by which they are discharged upon the apron L.

"The sticks as they are carried around by the endless chain of clamps have their lower ends brought even by the hammer M^1, which descends on the tops of them, and forces down any that may project upward above a proper height, and they have their lower ends dipped in the sulphur in the basin P^1, and afterwards they are covered by a roller z^1 with the igniting compound in the basin R^1, the roller z^1 being made to rotate within the basin R^1. The sulphur and igniting compounds are kept in a fluid state by the flue S^1. A roller x^1 serves to dip or depress the ends of the match sticks into the basin P^1.

"Another device may be employed in lieu of the cams I J for moving the endless chain of clamps C; for instance, the said endless chain of clamps may pass around pulleys a^2 operated intermittently from the driving shaft F by any proper means, and the clamps may be opened at the proper time time to receive the match sticks, and also to allow them to be discharged by means of wedges b^2 (Fig. 89), which are worked by a cam c^2."

Statistics of the Match trade.

This branch of industry, which is not much more than twenty-five years old, has been developed with a rapidity which is scarcely credible. Phosphorus matches appear to have been introduced simultaneously in different countries about the year 1834. In Germany they were first manufactured on a large scale in the Grand Duchy of Hesse, especially in Darmstadt, whence the manufacture was gradually extended throughout Germany; but its progress was at first very slow, the lucifer-match having been prohibited until the year 1840 in Bavaria, Brunswick, Hanover, and several other states, on account of the alleged increased risk of fire resulting from its use. At present, however, there are manufactories established in Vienna, Prague, Berlin, Ulm, Nuremberg, and numerous other German towns.

The manufacture appears to have taken its leading development in Austria, and forms the most important part of the trade

of Austria with Chili. The matches manufactured in Austria in the year 1849, amounted to 50,000 cwt. of which four-fifths were consumed in the country, and one-fifth was exported. From Trieste, 3787 cwt. were shipped, viz., to

Turkey	1,266 cwt.
Greece	596 „
Malta	492 „
Egypt	382 „
Ionian Islands	336 „
Naples	225 „
Other countries	530 „
	3,787

That the export trade of Austria was rapidly increasing when these returns were made out, appears from the following statement of the quantities shipped on the Elba during the three years, viz.,

In 1848	286 cwt.
„ 1849	790 „
„ 1850	1,860 „

It is estimated that of the total production of matches in Austria, one-third is manufactured in Bohemia, and two-thirds in the factories of Vienna and its vicinity. In illustration of the quantities of the different materials employed, it may be stated that a Bohemian manufactory, employing 100 work-people, produces annually about 200,000 boxes, each containing 5,000 matches: it consumes annually 25 cwt. of nitre, 6½ cwt. of phosphorus, and 300 cwt. of sulphur. Calculating on these data the total amount of materials consumed in all Austria, the following numbers are obtained :—

Nitre	1,250 cwt.
Phosphorus	325 „
Sulphur	15,000 „

The quantity of soft wood consumed annually amounts to 5000 *klafters* or fathoms, a large portion of which is manufactured into splints at Budweis and sent to Vienna. About 50,000 millions of single matches are annually produced in Austria.*

According to Payen (Chimie Industrielle, 4me ed. 1859, ii.

* The statistics above given of the Austrian match-trade are taken from the "Reports of the Juries" of the Exhibition of 1851.

551), the manufacture of lucifer-matches occupies 1500 work-people, chiefly women and children, in Paris alone, and from 800 to 1000 in the rest of France. The total annual produce amounts to 2000 millions of boxes, representing a value of 3,800,000 francs. The quantity of phosphorus annually consumed in the manufacture is 36,000 kilogrammes (about 30 tons), while the quantity consumed for all other purposes scarcely amounts to 500 kilogrammes.

In this country, the annual consumption of phosphorus is 8 tons, and of chlorate of potash nearly 26 tons. A London manufacturer examined, a few years ago, before the Children's Employment Commission, stated that he used £1,000 worth of American pine yearly in making boxes, and he estimated the *weekly* production in London at 12,000 to 15,000 gross of boxes, each containing 50 matches, so that the *annual* production of the metropolis amounts to 5000 millions of matches.

At Messrs. Dixon's works, at Newton Heath, the weekly consumption of sulphur is one ton, and in the year 1855 the consumption of chlorate of potash amounted to between 4 and 5 tons, and of glue to 12 tons. About 300 people are employed on the premises, and as a great quantity of work is sent out to be performed by women and children in their own cottages, probably not fewer than 450 to 500 persons are maintained by work from this firm. The timber-yard in which the material is piled up, awaiting its turn for the saw is from two to three acres in extent, and is covered by the huge trunks of American red and white pine, worth on an average, in its various stages, about £10,000. The average daily production of the finished article at Messrs. Dixon's works fluctuates between 6,000,000 and 9,000,000. The more certain average of the week is 43,000,000, so that allowing two full weeks in the year for holidays, the produce of the remaining fifty weeks will amount to 2160 millions of matches.

The total production of lucifer-matches in Great Britain is estimated (or was estimated in 1856) at 40 millions per day, and the quantity imported from foreign countries at about 200 millions, making the total consumption 240 millions per day, or about *eight matches per day per head of the whole population.* This result agrees very nearly with information supplied from Belgium.

Formerly the greater part of the phosphorus used in the

lucifer manufactories of this country was imported from abroad; but it will be seen from the following table (taken from the "Reports of the Juries," 1851), that this substance is now manufactured within the British dominions in quantity sufficient to supply the entire demand.

Value of the imports of phosphorus into the United Kingdom.

From 9th July.	From Denmark.	From the Hanseatic Towns.	From Holland.	From France.	From all parts.
1842	£1	£45	£14	£1102	£1162
1843	...	1	20	2349	2370
1844	...	...	83	2484	2567
1845	...	...	25	1474	1499
1846	...	12	...	619	631
1847	...	22	52	498	572
1848	...	16	15	149	180
1849	...	29	60	33	122
1850	...	2	...	1	3

HYPOSULPHITE OF SODA.

$$NaO.S^2O^2 + 5\,HO.$$

This salt crystallizes from solutions of moderate concentration, in large semitransparent oblique prisms belonging to the right prismatic system. It has a cool, somewhat bitter, and sulphurous taste; is unaltered by exposure to the air, and is neutral to test paper. When heated very carefully, the crystals fuse and lose nearly 36 per cent. of water, while the application of a higher temperature causes the separation of sulphur and leaves a mixture of sulphide of sodium and sulphate of soda. The solution absorbs oxygen very slowly from the air, deposits sulphur, and finally contains nothing but sulphate of soda.

Hyposulphite of soda may be produced by several processes, of which the following are the principal:

1. Crystallized carbonate of soda, dried, is mixed with about $\frac{1}{3}$ of its weight of sulphur and the mixture slowly fused and kept in a pasty state, with constant stirring, for some time. The

cooled mass is dissolved, digested with sulphur for some hours, and the solution, evaporated and set to crystallize, yields a quantity of this salt, but not enough to pay.

2. A stream of sulphurous acid gas is passed into a strong solution of carbonate of soda, to which fresh additions of the latter salt are constantly made. When the solution has become so strong that crystals of bisulphite of soda are copiously deposited in the bottom and on the sides of the vat, the addition of carbonate is stopped and the stream of gas allowed to pass until the last portions of that salt are decomposed, excess being however avoided. The liquor is then transferred to large boilers well covered, and digested with flowers of sulphur until it assumes a pale yellowish tint or becomes colourless. It is then set aside to crystallize, and yields an abundant crop of large crystals, which are purified by recrystallization.

The sulphurous acid employed in the last process may be conveniently generated by heating together in an earthenware, or, still better, in a cast-iron vessel, furnished with a bent leaden safety funnel and an exit pipe of the same material, a mixture of rectified oil of vitriol and fragments of charcoal, coke, sulphur, or chips, the gas evolved being passed, as an additional precaution, through a wash bottle containing water or sulphuric acid.

Or it may be produced on a larger and more economical scale by the slow combustion of sulphur in a furnace of sheet iron, or other material, through which a gentle current of air is made to pass by means of an aspiratory apparatus arranged at the other end. Or, finally, the arrangement may be so made that the sulphur is contained in a close vessel, provided with a man-lid or opening, by which fresh material may be introduced, and through which a current of air is continually forced by a pump, worked by the steam engine, or other convenient power,—the whole combination resembling that employed in some of the French sugar refineries for generating a powerful stream of carbonic acid gas, used to decompose the saccharate of lime in Rousseau's and other processes.

3. A large proportion of the hyposulphite of soda now consumed in Great Britain, as well as a large quantity exported to the markets both of the Old and New World, is manufactured at the Walker Alkali Works, Newcastle on Tyne, by Losh's patent process.

The above-mentioned patent was granted to William Septimus Losh, 21st July, 1852, for improvements in obtaining salts of soda by treating the waste residuum of the ordinary process of soda-making (commonly known as alkali-waste, tank-stuff, or vat residuum) or solutions thereof, with soda, which will combine with the sulphurous portions of the same, thereby producing certain salts of soda, named Hyposulphite of soda and Sulphite of soda." The mode of operation is described as follows:—"Take Alkali waste, or the residuum produced in the ordinary process of soda making, lay it up in heaps as it comes from the vats. After remaining a few days exposed to the atmosphere, a saline efflorescence will be produced on the heaps. This effect will be produced after a week's exposure. At the expiration of this time, the alkali waste is to be transferred to iron vats, where water is run upon it to dissolve the whole or greater part of the sulphurous compounds contained in the alkali waste. The materials are then left to settle, and the clear supernatant liquid is run into another vat, where a solution of caustic soda or carbonate of soda is added until salts of soda are formed. The salts of soda thus formed in solution are obtained in a solid state by evaporating the liquid up to suitable strength and then crystallizing." Incredible as it may appear to those who are familiar with the usual impurity of commercial products elaborated on the great scale, the salt manufactured at these works is chemically pure.

Hyposulphite and Sulphite have also been manufactured in large quantity, since 1847, at the Bonnington Chemical Works, near Edinburgh.

The use of hyposulphite of soda in fixing photographic impressions by dissolving out the undecomposed salts of silver, is well known. A more recent and far more extensive application consists in its employment as an "antichlor" in the paper manufacture.

It is computed that in England alone the amount consumed in photographic operations, is not less than 200 tons per annum, the value of which at wholesale prices, probably not one half of the sum actually paid by the final consumer, would be from £8,000 to £10,000, while a far larger quantity is employed in paper manufacture.

The application of bleaching powder to the decoloration of rags from which paper is fabricated, involves a somewhat pro-

longed exposure to this re-agent; and in consequence, the perfect removal of all excess becomes a matter of much difficulty, and in some cases practically impossible: the frequent result is a gradual decay or rotting of the goods after storeage, fading of the coloured qualities, and in some instances partial obliteration of documents written upon paper thus imperfectly prepared, while a not less serious evil is the injury of the delicate machinery of the manufactory.

An excessive amount of washing did indeed obviate the difficulty, but involved a serious waste of material. The only effectual remedy is the application, subsequently to the bleaching, of a reagent capable of effecting the complete abstraction of all traces of chlorine that may have been left in the pores of the paper, the product formed in this last process being itself readily removed by washing.

Hyposulphite of soda completely fulfils these requirements, and furthermore, the paper produced is found to be of whiter and finer quality than can be obtained without the use of "antichlor," while the danger of injury to the machinery is wholly obviated.

The bleached and washed pulp is tested for traces of chlorine by paper prepared with the usual mixture of iodide of potassium and starch. The intense blue of iodide of starch instantly indicates the presence of chlorine, and the necessity of further addition of "antichlor," of which, however, an accidental excess has no injurious effect.

A patent was granted in 1847 to Mr. Henry Donkin, an eminent manufacturer of paper-makers' machinery, &c., at Bermondsey, for the use of bisulphite of soda as an "antichlor," and this substance was used largely until 1853, when the hyposulphite, from its cheapness and greater efficacy (its practical value being just double that of the bi-sulphite) superseded it.

The quantity of hyposulphite used by the paper-makers in the pulp-engine, after bleaching, is about 1½ to 2oz. to each cwt. of pulp.

Hyposulphite of soda is also coming into use among the bleachers of Manchester, &c.

It has been recently employed in large quantities for producing sulphurous acid, being cheaper and more manageable than the old plans of burning sulphur, &c. Saturated solutions of sulphurous acid are made by dissolving the hyposulphite in cold

water, adding the equivalent of oil of vitriol and agitating. Sulphur is then precipitated and sulphurous acid is dissolved. This process was also introduced by Mr. Losh.

The total quantity of the salt now manufactured in England is about 250 tons per annum: but, as its uses are being rapidly multiplied, it will soon far exceed this amount.

BORAX.

The salt which is sold and consumed under this name* is the biborate of soda ($NaO . 2BO^3$), which, with 5 or 10 atoms of water of crystallization, forms the two kinds of crystallized borax of commerce. That which contains 5 atoms of water ($NaO . 2BO^3 + 5$ aq.), is called octohedral borax, on account of the octohedral form of the crystals, and is the rarer of the two; it contains, in its pure state, 30 per cent. water. This salt was first distinguished by Payen, from the well-known variety with 10 atoms of water ($NaO . 2BO^3 + 10$ aq.), which crystallizes in prisms. The water, in the former amounts to 30·9; in the latter to 47·2 per cent.

Both varieties, when exposed to the action of heat, part with all their water, and expand into a vesicular mass, before melting to a clear glass, which possesses the important property of dissolving most of the metallic oxides with the assumption of characteristic colours; it also adheres to the bright surface of metals, protecting them when covered with it, even at a red heat, from the oxidizing action of the air. It is this property which renders borax so valuable as a flux, as glass, and, above all, as a means of facilitating the soldering and welding of metals. Borax is also used in medicine.

The borax of commerce is derived from two different sources. In former times, the mineral as it occurs in nature, after being purified, was the only known borax; but this has now been almost completely superseded by artificial borax, prepared from volcanic

* Borax is derived from the Arabian word *baurach*; Agricola calls Borax *Chrysocolla*, gold-cement, on account of the use to which it is applied in soldering gold.

boracic acid and soda, a branch of manufacture which has been mainly dependent upon the vast extension of the soda trade.

Artificial Borax.—Occurrence of Boracic Acid.—This manufacture, which French industry has cultivated with such signal success, is carried on upon so large a scale in France, that nearly the whole amount of boracic acid is there consumed which the north of Italy can supply. The occurrence of this acid in the grand duchy of Tuscany, which abounds in volcanic products, is as peculiar, interesting, and important, as the method of procuring it. The boracic acid, in those volcanic districts, which extend 35 to 40 miles, is brought from the interior of the earth by numerous jets of vapour, which are there called *suffioni*. These suffioni are announced from a great distance by the ascent of thick columns of vapour, which often rise to a considerable height. The entire surface of the volcanic district, consisting of chalk and marl, is subject to constant shocks, caused by subterranean agencies; columns of boiling water are frequently projected into the air, which is strongly impregnated, at the same time, with sulphurous vapour,* and the whole presents a scene of vast desolation. In some parts, the apertures whence the vapours issue are freely exposed; in others, they are covered by standing water, which, by the constant agitation of the soil and of the vapour, become converted into small muddy lakes (lagoons).

It is well known that boracic acid forms an exception to the general rule observed by those bodies which are fixed when melted in the fire, and to which class it belongs. It volatilizes in such quantity with the aqueous vapour from a boiling solution, as to render its quantitative estimation very inaccurate under such circumstances. The presence of boracic acid in the suffioni is evidently accounted for in this manner. It is, nevertheless, remarkable, that, by simple condensation of the current of gas and vapour, no boracic acid can be obtained, a fact which can only be explained by the extremely minute quantity held in solution. This quantity, however, is considerably increased when a lake covers the aperture of the suffioni. It would appear, from the observations of Payen and Bowring, whom we have to thank for the best accounts upon this subject, that the boracic acid is brought up, by the water of the lakes which occasionally enters the mouths of the suffioni; for the acid, being probably deposited before the vapour reaches the surface, requires the aid of more water to dissolve it. The real source of the boracic acid in the suffioni is

* Sulphuretted hydrogen, according to M. Larderel.

totally unknown, and all that can be stated upon the subject is the theoretical opinion of Dumas. This philosopher has endeavoured to explain the phenomena by the assumption of a very deep bed of sulphide of boron, with which the water of the lakes or of the sea comes into contact. In this case, boracic acid and sulphuretted hydrogen would be produced, with great evolution of heat, and these would be accompanied by the products of decomposition of the other constituents of the water, which really is the case, as far as hydrochloric acid and ammonia are concerned. The remaining phenomena are then easily explained by the contact of the products of decomposition with deposits of limestone and clay. At a certain distance above the scene of decomposition, the boracic acid may be deposited, and according as the water of the lagoons does or does not reach it, it will be taken up, and pass off in the vapour, or will be left unvolatilized.

Payen found that these suffioni contain, at a temperature between 97° and 100° C. (174° and 212° Fah.), much solid matter carried up mechanically, besides permanent gases and aqueous vapour. The mixture of permanent gases consists, in 100 parts, of 57·3 carbonic acid, 34·81 nitrogen, 6·57 oxygen, 1·32 sulphuretted hydrogen, whence it is evident that atmospheric air must have access, and take part in the decomposition.

The oxygen appears to be merely accidental, depending on the admixture of a small quantity of air with the gas; for other experimenters have not found it. MM. Ch. Saint Claire Deville and F. Leblanc have observed that all the gaseous emanations contain free hydrogen and a gaseous hydrocarbon. The following is the result of the analysis of several emanations from Larderello:—

	Suffioni.		
	Lowest.		Highest.
Sulphuretted hydrogen	4·1	3·7	85·1
Carbonic acid	91·6	90·7	
Oxygen	0	0	2·7
Nitrogen and combustible gas	4·3	5·6	12·2
	100·0	100·0	100·0

Absorbable Gas.

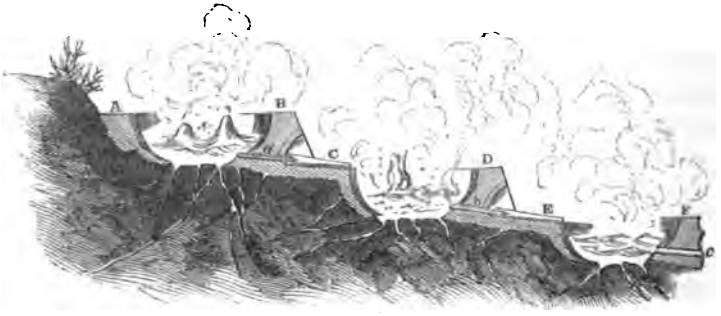
Nitrogen	43·35
Hydrogen	28.56
Marsh gas	28·09
	100·00

When all due precautions were taken for collecting the sulphuretted hydrogen, MM. Deville and Leblanc found 6·4 SH for 93·6 CO^2.

The origin of the gaseous hydrocarbon is doubtless related to that of the essential oil which Payen has found in crude boracic acid, and is to be found in the decomposition and volatilization of the organic matters contained in the water, by whose action on the sulphide of boron the gaseous emanations are produced. (Payen, *Précis de Chimie Industrielle*, 1859, i. 426.)

In the condensable portion of the vapours are found clay, sulphate of lime, ammonia, sulphate of alumina, protosulphate of iron, muriatic acid, and organic matter having the smell of sea fish, with little or no boracic acid. Sulphur is deposited in all parts where there are crevices and pores in the soil.

FIG. 90.



Method of obtaining Boracic Acid.—In this district there are ten manufactories, at distances of a mile to a mile and a half from each other; these arè—Larderello, Monte Cerboli, San Federigo, Castel Nuovo, Sasso, Monte Rotondo, Lustignano, Serrazano, Lago, and San Eduardo, all situated at the foot of a moderate eminence, from whence jets of vapour arise in different directions. The process is founded upon the observation already mentioned, that the acid volatilizes with the vapour of water.

The Lagoons.—The arrangement consists of a series of basins in connection with each other (artificial lagoons), constructed of rough brickwork in a circular form, and lined with clay, round the mouths of one or more of the larger suffioni. The diameter of these basins varies from 16 or 20 feet in the smaller, to 60 or 80 feet in the larger, and they are from 6 to 10 feet deep.*

* M. Larderel states that the dimensions of the lagoons differ consider-

Fig. 90 represents the manner in which they are arranged in terraces on the side of the hill. On the lower side of each basin is an arch, by means of which the plugs of the tubes *a b* are accessible, and by opening these, the water from the higher flows into the lower lagoon through the channels C E. These artificial basins, of which there are six or eight, serve to saturate with boracic acid the water of neighbouring springs or brooks, with which the uppermost A is supplied, until it is sufficiently impregnated to pay for the expense of working.

When the fresh water arrives at the lagoon A B, it is partially imbibed, the vapour being at first condensed; but as soon as it has attained the temperature of the vapour, it is again evolved, and the whole of the lagoon is kept in constant agitation by the current of gas at a temperature of from 93° to 95° C. (199° to 203° F.). At the expiration of 24 hours, during which time it has been kept in this state, the plug is removed, and the water allowed to flow into basin C D, where the same operation is repeated. The fluid becomes charged with some more boracic acid and other substances, the quantity of which is again augmented in the basin E F, and in those which succeed it, every 24 hours. When the solution has thus traversed 6 or 8 of the lagoons, it is found to have taken up about ½ per cent. of boracic acid, and its specific gravity has been raised to 1·007 or 1·010.*

Clarification.—From the last lagoon G H, Figs. 91 and 92, the solution is received in a large clarifying vessel I, called a "*Vasco*," composed of brick work, 24 feet square, and 4 feet deep, in which, during one night, the greater part of the mud is deposited, and from which the surface liquid is drawn off into a reservoir J for the supply of the evaporating pans.

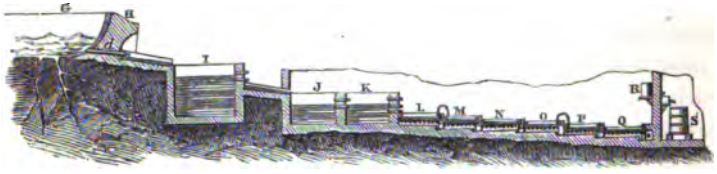
Evaporation.—The vessels for evaporation are leaden pans (Figs. 91, 92), similar to those used in the preparation of sulphuric acid; they are 12 feet square, and 14 inches deep. Seven of these pans, placed side by side, form one connected

ably; the smaller ones, he says, are 100 feet in circumference and 7 feet deep, but there are some which are from 500 to 1,000 feet in circumference, and 15 to 20 feet deep. There are generally several, from 3 to 15, sources in the latter. The depth and surface of these basins must also be in a certain relation to the force of the column of vapour; if the depth and surface are too great, and the basin contains too much water, the vapour encounters great opposition, and frequently seeks another outlet.

* The lagoons are now emptied every day, as the amount of boracic acid (1 to 1½, rarely 2 per cent.) is not increased by remaining there longer.

whole, and have together a capacity of nearly 3000 cubic feet. The single pans* are situated in the manner of terraces one above the other upon a wooden scaffolding, in such a

FIG. 91.



manner that the first four form the upper range, the following two the second, and the lowest pan the last. No fire is employed, but the heat requisite for evaporation is obtained from one or more of the jets of steam, enclosed in pipes, and

FIG. 92.

conducted between the foundation and the bottoms of the pans. Thus, not only the highly valuable crude material itself, but at the same time heat for concentrating it, is in these districts supplied by nature; and indeed, if it were not for these remarkably favourable circumstances, the production of boracic acid would be almost an impossibility in a country where fuel is so very scarce. The presence of boracic acid in the vapours of the suffioni of Tuscany, was clearly shown by Franz Höfer, Apothecary to the Court of Florence, in the year 1778, who mentions, in a pamphlet, "Upon the sedative salts found in Tuscany," that this acid affords, with soda, a kind of borax exceeding the ordinary borax in purity. Neither this, nor Mascagni's more recent hints, prevailed in rousing the indolence of the inhabitants of those districts to more than a few unsuccessful undertakings. Their bad speculations overstocked the market, and brought ruin upon themselves. The improvements of Ciaschi at the beginning of the present century, who introduced the consecutive saturation in the lagoons, and

* To save space only six are represented in the figures.

those of Larderel, his successor, in 1817, at that time the proprietor of all the lagoons, who carried out the idea of using steam heat instead of expensive fuel, first raised this valuable branch of industry to its full extent. In the year 1818, the same district of Monte Cerboli, which now produces a yearly income of £4000, would have been let for a rent of £6 10s. per annum.

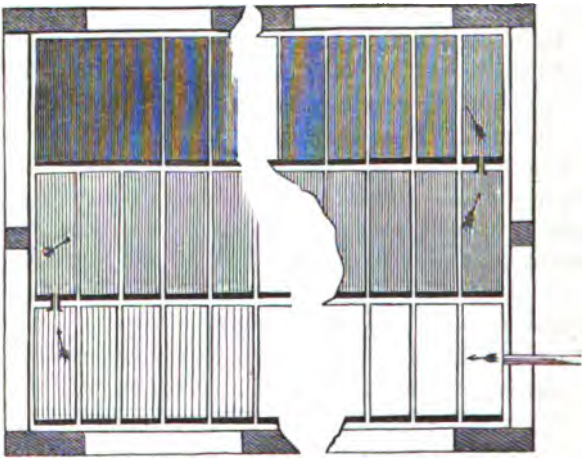
When the four upper pans, L M N O, have been filled with fluid from the reservoirs, and this has remained in them during 24 hours, the half of it will have been evaporated, and the pair of pans below will just be large enough to hold the remaining half. This, therefore, is drawn off, and the upper pans are supplied with a fresh portion from the clarifier. At the expiration of another 24 hours, the half is again evaporated, and the fluid is reduced to ¼th of its original volume; it now consists of a much stronger solution of boracic acid, and may be brought into the lowest vessel Q, where the evaporation is completed.* The process, as here described, undergoes no interruption; the lye from each pair of pans is only removed to make room for a fresh charge of weaker solution. During evaporation, much sulphate of lime is deposited in the pans, which must be removed from time to time by rakes. In the same manner as the fluid becomes richer by the addition of boracic acid in the lagoons, so it is still further enriched in the pans, by the evaporation of the water, until at length the same fluid in which it was hardly possible to discern the presence of boracic acid, has become converted in the lowest pans into a solution, which, when mixed with the mother-liquor of a former crystallization, has a specific gravity of 1·07 to 1·08.

The arrangement of the evaporating pans at Larderello is somewhat different: it is shown in Fig. 93. Three parallel series of shallow leaden divisions are placed in a line, each being a third of an inch below the one before it, from which it is separated only by a leaden partition half an inch in breadth and depth. The divisions are placed transversely and are 6 ft. by 22 inches.

* The evaporation lasts altogether 62 hours. At present, there are 400 evaporating pans in operation, each of 10 feet surface, besides which there are several others, with diaphragms arranged in rows, 300 feet in length, in which the water, constantly evaporating, flows slowly through the different divisions until it becomes sufficiently concentrated. More than 1200 lbs. of water are thus evaporated daily.

They are arranged under a shed to keep off the rain, but open at the sides, so as not to impede the evaporation. The water is turned on by a tap from the tank into the first division in regulated quantities; it then flows on from one division to another till, arriving at the bottom of the building, it passes into the second row of divisions, and finally back through the last series into the diagonal corner, where there is a large and deep reservoir

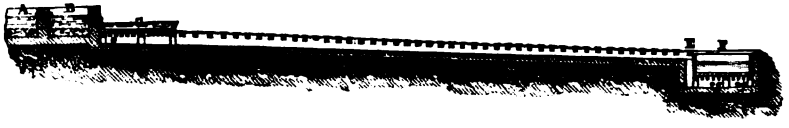
FIG. 93.



called the *Caldajo a sale*, from which it is conducted along a wooden pipe to the crystallizing house.

Another form of apparatus for the evaporation is represented in Fig. 94. The liquid, after being deposited successively in the vasques A B, is drawn off from the latter into a shallow

FIG. 94.



boiler C, from which it is made to run slowly over an inclined sheet of lead D E about 150 ft. long, and having corrugations on

its surface, which form a series of small channels. The liquid, in running over this surface, gradually evaporates, and the solution ultimately reaches the basin F, at a degree of concentration fit for immediate crystallization. Heat is supplied by the vapour of one of the suffioni introduced under the basin F, and carried up under the sheet of lead to C. This mode of evaporation is easier than that before described, and does not introduce so large a proportion of lead into the solution.

Crystallization.—The mixture of fresh, saturated solution and mother-liquor is now taken from the pans, and is brought into the vessels A A A, Fig. 95. These are round wooden tubs, lined with lead; they are 4 feet high, 31 inches in diameter, and have a capacity of about 8 cubic feet. They are so arranged, that the mother-liquor, running into the vessels B, may be easily withdrawn, and returned to the lowest pans. The small lamellar crystals are placed in baskets C to drain, and whilst still moist, are spread out in a layer 1½ inch in thickness on the floor E E of the drying chamber D (Fig. 96). The floor of this chamber is double, and a jet of steam entering at F is made to circulate below the one floor, in the space left between it and the other. The chamber is accessible by the door G. The dry acid is conveyed in the first instance to Leghorn, and from thence, by sea, to its destination.

FIG. 95.

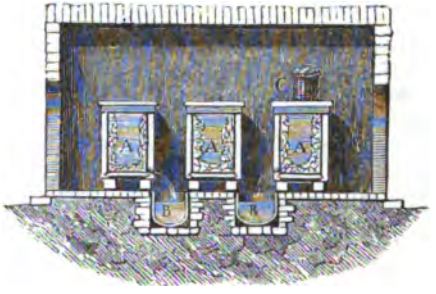
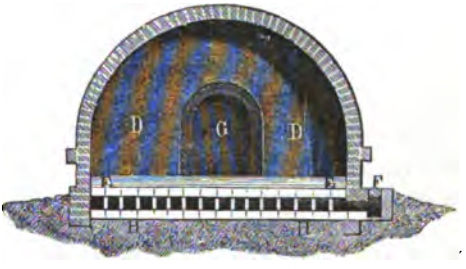


FIG. 96.



Constituents of the Crude Acid.—Wittstein gives as the correct analysis of commercial boracic acid in 100 parts:

Crystallized boracic acid	76·494		91·576
Sulphuric acid combined with boracic acid	1·322	Sulphate of potash	0·369
Sulphate of ammonia	8·508	„ „ manganese	trace
„ „ magnesia	2·632	Chloride of ammonium	0·298
„ „ lime	1·018	Silica	1·200
„ „ soda	0·917	Water of crystallization in the salts	6·557
„ „ sesquiox. iron	0·365	Organic matter containing nitrogen	trace
„ „ alumina	0·320		
	91·576		100·000

According to Payen (*Précis* 1859, i. 431) the composition of crude boracic acid exhibits the following varieties:—

Crystallized boracic acid ($BO^3.3HO$)	74·0 to 84·00	(=41·5 BO^3)
Hygroscopic water	7·0 „ 5·75	
Sulphate of ammonia and magnesia*	14·0 „ 8·00	
Sulphate of lime, clay, sand, sulphur	2·4 „ 1·25	
Azotised organic matter, essential oil, having the odour of sea-water, chloride of iron, chloride of ammonium, hydrochloric acid, &c.	2·6 „ 1·00	
	100·0	100·00

The following analyses of boracic acid from Italy are by Richardson and Browell:—

Boracic acid	41·57	36·38	42·74	33·24
Soda	2·35	1·05	·97	·98
Chloride sodium	·30	·36	·20	·21
Sulphate soda	11·07	13·48	8·25	13·75
Sulphate lime	·68	2·31	1·83	3·20
Sulphate magnesia	1·07			
Water, ammonia, and organic matter	41·50	45·25	45·00	47·50
Insoluble matter	·66	1·17	1.01	1·12
	99·20	100·00	100·00	100·00

Hence, it appears, that upon the whole, although the best is retained for the manufacture of borax in Leghorn, a very impure

* The sulphates contained in crude boracic acid occasion a loss to the manufacturer of borax, inasmuch as they are converted into sulphate of soda at the expense of an equivalent quantity of carbonate of soda, the commercial value of which is about double that of the sulphates.

product is obtained. This would not be the case to such an extent, if the mother liquor, instead of being returned into the pan, were evaporated again, and after the separation of the boracic acid were used for some other purpose—in the manufacture of alum, for instance. The experience of the French manufacturers likewise tends to prove, that the impurities in the acid from Tuscany increase from year to year, so that the quantity of foreign matters, which, at first, was only from 8 to 10 per cent., has gradually increased to 18·23 (as in Wittstein's analysis), and even to 25 per cent.; a fact which is probably to be accounted for by the increasing disintegration of the earthy strata by the action of the currents of steam.

Each set of 14 pans produces, by the process described, after three times 24 hours' evaporation, 180 lbs. of crystallized acid, which presupposes the removal of 36,000 lbs. of water. From the statements made at vol. i, pt. 1, p. 172, it appears, that to evaporate 4·7 lbs. of water, 1 lb. of ordinary fire-wood is required. In Tuscany, the yearly produce is now 15,000 cwts. of acid (Payen); the water evaporated must, therefore, amount at least to 1·6 millions of cwts., which, under ordinary circumstances, would require 21,000 stacks of wood (1 stack = 100 cubic feet, containing about $\frac{7}{10}$ths of solid wood). According to Bowring, the yearly produce since 1836 has been nearly 3 millions of pounds; therefore, double the former average.

The following statement of the production of boracic acid since the year 1818, is given by Count Larderel:*

Years.	Tons.	Cwt.	Years.	Tons.	Cwt.
From 1818 to 1828	521	16	1849	1,043	13
„ 1829 „ 1838	4,870	6	1850	1,043	13
1839	748	13	1851	1,140	0
1840	878	13	1852	1,156	19
1841	886	6	1853	1,208	19
1842	923	15	1854	1,319	7
1843	923	16	1855	1,332	19
1844	923	16	1856	1,427	1
1845	923	15	1857	1,711	4
1846	1,043	13	1858	2,026	10
1847	1,043	13	1859	1,830	18
1848	1,043	13			
			Total	29,972	18
			Or Tuscan pounds	86,155	917

* See a paper on the production of boracic acid, by W. P. Jervis, F.G.S.,

The Custom House returns show that the importation of Boracic acid from Tuscany into England has been in:—

Year.	Quantities.		Value.
	Tons.	Cwt.	£
1852	1,925	1	106,691
1853	1,038	8	121,163
1854	1,185	9	110,264
1855	1,338	16	87,192
1856	1,253	0	73,157
1857	1,245	12	94,846

Valuation.—The method of estimating the value of a sample of commercial boracic acid is very simple. The excess of water above that which is essential to the crystallized acid (BO^3. 3HO) is determined by desiccation at 40°—45° C. (104°—113° F.) or in vacuo. The boracic acid is then dissolved, but with alcohol, and the weight of the residue gives within 1 per cent. the amount of foreign matters, consisting of chlorides, sulphates, and organic matter. The amount of pure boracic acid may be determined directly by neutralising the concentrated alcoholic solution with soda, so as to transform it into borax ($2BO^3$. NaO), washing the dried residue with alcohol, and weighing ·100 parts of this salt, correspond to 53·9 parts of anhydrous boracic acid.

Uses of Boracic Acid.—The chief use of this acid is in the manufacture of borax, which will be described immediately. It is also used in the composition of certain vitrifiable compounds, and is introduced in the lining of the earthenware boxes in which porcelain is baked, in order that it may be converted into vapour which glazes the porcelain. With 100 parts of water, and a fourth of its weight of sulphuric acid, it forms a solution for dipping the wicks of stearine candles, its use being to cause the wicks to curve in burning, and at the same time to vitrefy the ash. Boracic acid is likewise used in the preparation of *soluble cream of tartar*, $C^8H^4O^{12}$. KO . BO^3, and for decomposing certain silicates, for the purpose of estimating the alkalies. (Payen.)

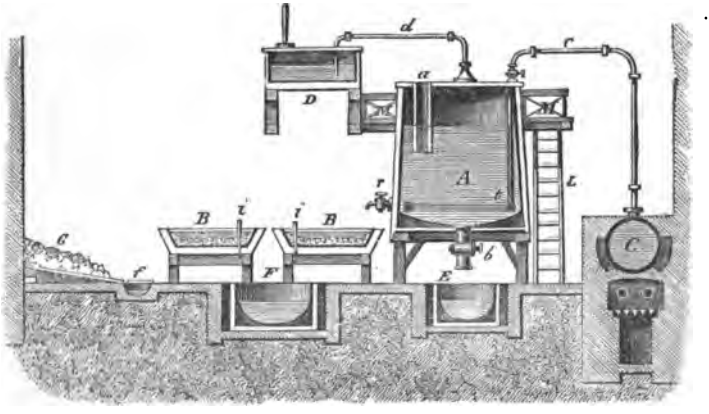
PREPARATION OF BORAX.

100 parts of commercial boracic acid require for saturation

in the "Journal of the Society of Arts" (25th May, 1860). This paper contains an interesting account of the history of the manufacture, and a graphic description of the locality.

120 parts of crystallized soda, or an equivalent quantity of salts of soda. Vats lined with lead *A*, Fig. 97, are used for this purpose, precisely similar to those employed in the manufacture of stearic acid. The steam for heating enters the vat by a pipe *c* from the boiler *C;* the tube extends to the bottom of the vat, and terminates in a horizontal circular bend *t*, which is pierced with holes for the escape of the vapour. Two cocks, one *r* at the side, and another *b* at the lowest part of the arched bottom, serve to empty the vessel; the aperture *a* with its tube is for the introduction of the charge; the whole is closed with a cover to prevent any loss of heat. Ladders *L*, and platforms *M*, are attached to the apparatus, for the convenience of ascending to the upper parts. In the beginning, nothing but the mother-liquor from the last crystallization is placed in the vat, to which the soda and water are added in sufficient quantity to produce about 200 lbs, including that from the condensation of the vapour. When the soda is dissolved, and the temperature of the fluid has risen to 100° C. (212° F.), the boracic acid in coarse powder is introduced, and, to prevent loss from effervescence, in quantities of 10 lbs. at a time. In this operation, the boracic acid is not only neutralized, but a considerable loss of soda is occasioned by the sulphates and chlorides, which are mixed with it. Thus, sulphate of soda and some common salt are produced, also carbonate of lime, carbonate of magnesia, hydrated oxide of iron, and principally carbonate of

FIG. 97.



ammonia. In an open vessel, the latter would volatilize with the aqueous vapour; to prevent the loss of this valuable secondary

product, the apparatus is so constructed, that the gases and vapours shall pass through a tube *d* in the lid, to a neighbouring condenser *D*, and pass through sulphuric acid. The carbonic acid is thus set free, and all the ammonia remains as sulphate of ammonia. When all the acid has been added, the solution must indicate 21° Beaumé (1·166 sp. gr.), and its temperature must be raised to the boiling point, to 105° C. (221° F.); the steam is then shut off, the aperture *a* is closed, and the solution allowed to remain at rest for 12 hours. As soon as the lye has become sufficiently clear, it is drawn off by the cock *r*, into the shallow crystallizing vessels *B B*, which are lined with lead; the deposit falls through *b* into *E*, where it is washed and then thrown away. When the crystallization is finished in the vessels *B B*, the leaden plugs *i i* are removed, and the mother-liquor collects in the common reservoir *F*. It has already been stated, that this is returned to the vat *A*, for the next saturating process with boracic acid; but at last the foreign salts accumulate to such an extent, that they must be separated in some other manner. The borax is allowed to crystallize at a temperature of 33° C. (92° F.), when all the other salts remain dissolved, and then by a subsequent evaporation the sulphates of soda and magnesia are obtained.*

In some works, the proper proportions of soda, salts, and crude boracic acid are carefully mixed and calcined at a low heat; the mass is treated with water; and the ordinary process followed for the crystallization of the borax.

The sulphate of soda having its maximum of solubility at 33° C. (91·4° F.) will not have begun to crystallize at the time when the crystallization of the borax is nearly complete. After the sulphate of soda has crystallized out, the mother-liquor concentrated by evaporation yields a second crystallization of borax; and the mother-liquor separated from the crystals at 33° C. again yields sulphate of soda. The remaining liquid, which is still more impure, will probably contain such a quantity of chloride of sodium as to render it necessary to precipitate that salt by boiling the solution;

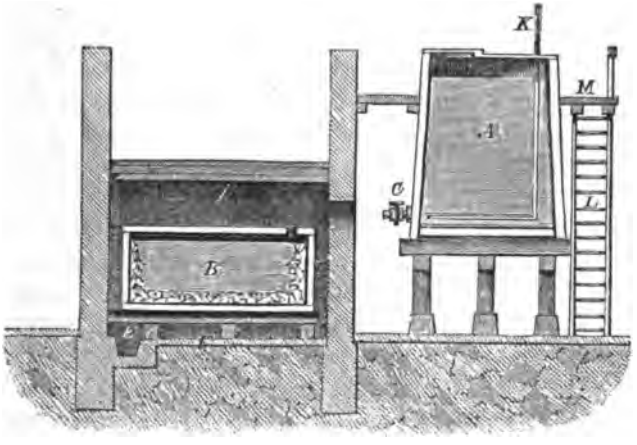
* This process is somewhat differently described by M. Koehnke (see Chem. Gaz., vol. iii. 131). A solution of caustic soda is prepared, amounting to about 170 lbs. of 1·090 to 1·095 sp. gr.; to this 40 lbs. of good Tuscan boracic acid are added, and the whole is boiled until the lye is reduced to 120 or 125 lbs., or indicates 1·175 to 1·180 sp. gr. Upon this the liquid is poured boiling hot into a wooden tub, which is well surrounded with woollen cloths and straw, and carefully covered to retain the heat as long as possible, so that a good and regular crystallization may be effected.

after which the clear liquid still yields on cooling a small quantity of borax.

The sulphate of soda may either be purified by washing or by a second crystallization ; or to avoid the expense of purification, it may be sold, together with the small quantities of borate and carbonate of soda which it contains, to the glass-makers. The chloride of sodium, being less valuable for this purpose, is refined for culinary or other use. The crystallizable mother-liquors evaporated to dryness yield a saline residue applicable to glass-making.

Crystallization.—The crystals are detached from the vessels *B B* by means of chisels and hammers, and placed upon an inclined board *G*, where the remainder of the mother-liquor collects in the channel *f*. This first crop is much too impure, and also in other respects unfit for the market; it must consequently be recrystallized, which operation is performed in the apparatus, Fig. 98.

FIG. 98.



The small crystals from the waste are often redissolved with the crude borax, both being placed in a large vat *A*, which differs from that represented in Fig. 97, only by having larger dimensions and no cock at the bottom. The vat must be heated in the same manner by steam, and lined with lead, and be sufficiently large to contain at least 180 cwts. of borax. The crude borax and the waste are placed in an iron wire-basket, which hangs by a chain passing over a pulley just below the surface of the water

(see Saltpetre); all stirring is thus dispensed with. It is necessary to add about 4 per cent. more carbonate of soda to the crude borax, and steam is then allowed to enter, until the solution indicates 21° Beaumé. When this point has been attained, the whole solution is drawn off by the cock *C* into the crystallizing vessel *B*.*

As large crystals alone are saleable, and these can only be procured with difficulty, and by avoiding all agitation and rapid cooling, the arrangement of these growing cisterns is somewhat more complicated. They are constructed of stout boards lined internally with lead, covered with a closely fitting lid which is also lined with lead, and are placed in an external box, with which they are not in contact. The space between the two vessels is filled with small coal *H*, and the lid is covered with a triple layer of coarse woollen stuff, that the cooling process may be retarded as much as possible. The vessels must not be placed near each other, as the shaking occasioned by removing the salt from the one, would disturb the growth of the crystals in the other. The crystallization continues from 25 to 30 hours, according to the temperature of the atmosphere, and is finished when the thermometer in the interior stands at 25° or 30° C. (77° to 86° F.). The mother-liquor is then drawn off with wide syphons, as rapidly as possible. When all that can be removed by the syphons is separated, that which remains amongst the angles of the crystals is taken up by sponges, that no small crystals may deposit upon the large ones, and the whole is immediately covered, and left at rest for several hours. This is necessary, to avoid cracks and crevices in the crystals, which would be occasioned by the action of the cold air. The workman must not enter the vessel to remove the crystals, until the temperature of the interior has sunk to that of the surrounding air. The hewn cake of salt is then placed upon a table to be broken up into single crystals and picked over. The crystals which are sufficiently firm, and not too small, are then thrown into baskets with wide meshes, that the grains and dust may fall through, before they are packed.

In this process, common borax with 60 per cent. of water is always obtained from a lye of 1·166 density. If octohedral borax with 30 per cent. of water is required, the lye must have a density

* The floor *F* below this is smooth and inclined, and made of glazed stones, whence all that is spilt flows into the channel *E*.

of 30° B. (= 1·256 sp. gr.), and be evaporated at a temperature of 100° (212° F.), before it is introduced into the crystallizing vessels. Octohedral borax begins to form at a temperature of 79° C. (174° F.), and ceases at 56° (133° F.). At this temperature, the mother-liquor must be rapidly removed, or the crystals will become covered with a coating of ordinary borax. The crystals attach themselves so firmly to each other, that, in removing them, hard, sonorous plates of any size may be obtained.

A remarkable prejudice of the buyers, who call the octohedral variety melted borax, and think that they are buying the ordinary kind when the plates present the projecting points and angles of the crystals, obliges the manufacturer to remove with a hatchet this true indication of their purity, before sending the salt to the market.

In both cases, whether the one or other variety of crystals has been grown, the mother-liquor deposits, in the wide basins to which it has been removed, an abundant crop of prismatic borax, which, after being drained, is used for enamel coatings. This mass of small grained crystals, not having the stamp of purity upon it, is seldom to be met with in retail. The small size and want of firmness in the crystals of artificial borax, were in the first instance so prejudicial to its introduction, that it was necessary to imitate the exact outward appearance of Dutch borax (native purified, from Amsterdam), its brown color, the mode of packing it, the rubbed appearance of the crystals caused by land carriage, &c., with the greatest minuteness, in order to render it saleable.

Sautter * has patented a process for obtaining borax without the intervention of water. 38 parts of pure dry boracic acid are thoroughly mixed with 45 parts of crystallized carbonate of soda, in powder. This mixture is placed in a room heated to from 90° to 115° F., upon wooden planks, in layers of about an inch in thickness; this temperature is found sufficient to enable the boracic acid to expel the carbonic acid and the excess of water from the carbonate of soda, and perfect borax or borate of soda is said to be obtained.

Native Borax (*Tinkal*).—Native borax has been found in several localities, for instance, at Halberstadt, in Siebenbürgen, in the mines of Viquintizoa and Escapa in Peru, in Ceylon, in Tartary, in China, but more particularly in India and Thibet,

* Nov. 20th, 1843, No. 9734.

from whence the greater part of that used in the arts was obtained. According to Turner, the lakes which furnish the Indian borax are situated a few days' journey from Tezhoo-Lomboo; and the borax is found in great blocks on the shores and bottom of the stagnant salt lakes, whilst more towards the middle common salt is predominant. On the contrary, Blanc and Pater Rovato state, that these lakes of Thibet are situated amongst the mountains of that country, the most celebrated of them, called Necbal, being located in the Canton of Sumbul. The water is said to be distributed in sluices, until, by evaporation, it deposits salt, after which it is allowed to flow off. The crude native borax is called by the Indians, tinkal. It is impure, and has the form of distinct six-sided crystals, more or less flattened, and some lines in length; these are sometimes colourless, sometimes yellowish or green, and always covered with an earthy incrustation, which is fatty to the touch, and smells of soap.

This latter property is derived from a substance resembling soap, composed of soda and a fatty body surrounding the crystals. The fat can be separated by acids, and then assumes the appearance of a dark brown rancid oil, soluble in ether.

Analyses of Indian Borax.—Richardson and Browell.

Boracic acid	22·88	40·24	24·41
Soda	12·59	11·11	11·71
Chloride of Sodium	·92	·11	·21
Sulphate of Soda	·13	·49	2·84
Sulphate of Lime	1·36	·68	1·36
Insoluble matter	17·62	1·37	20·02
Water	44·50	46·00	39·45
	100·00	100·00	100·00

From a very ancient period, borax has been purified in the seaport towns, "*refined*," and more particularly in Venice (whence the appellation Venetian borax, which is equivalent to purified borax); at a later period, the process was introduced into the Dutch towns, for instance, at Amsterdam. Great pains have always been taken to keep the process secret; nevertheless two different methods of purification have become known.

In one of these, the impurities are separated by lime, the tinkal being softened in a small quantity of cold water, and

stirred about with the gradual addition of about 1 per cent. of slaked lime. The turbid lime-water is alternately poured off, and when the impurities have settled down on standing, the clear liquid is again poured upon the crystals, and this process is repeated several times. In this manner, the greater part of the soapy compound is removed, and what still remains is separated by dissolving the crystals in hot water, and adding about 2 per cent. of chloride of calcium. Chloride of sodium is produced, and an insoluble lime-soap, which is removed by straining, and the clear liquid is then evaporated to the consistence of 21° B.

The other process consists in placing the powdered tinkal in a tub with holes pierced in the bottom, and washing it with a solution of caustic soda of 1·034 sp. gr. as long as this passes through coloured. The lye makes the soapy matter much more soluble. After draining, the crystals are dissolved in water, and 12 per cent. of soda is added, which precipitates the foreign matters and earths; these must be strained off, and the lye evaporated to the consistence of 20° B.

In both cases, the crystallization is effected in wooden vessels lined with lead, and having the form of short inverted cones. This shape is preferable, because the deposit which may form collects in the lower narrow part, and does not interfere with the crystallization. The use of lime facilitates the clarification, but may occasion a loss by the formation of insoluble borate of lime, for which reason the use of it cannot be very strongly recommended. Commercial borax, compared with that obtained from tinkal, has, notwithstanding its greater purity, one particular fault, viz., that the crystals, when heated, split in the direction of their natural cleavage, fall to pieces and fly off from the part required to be soldered, by which means a loss is occasioned, and the work retarded. The very great precautions used in the crystallization, lessen this evil; but it is more effectually remedied by the addition of a small quantity of tinkal before recrystallization.

Valuation of Borax.—This is easily effected by the volumetric method of Gay-Lussac, which is based upon the fact that boracic acid added in any quantity to blue tincture of litmus changes the colour only to a purplish red or wine-red colour; whereas the smallest quantity of sulphuric acid, or any of the stronger acids, immediately produces a bright red tint. If, therefore, sulphuric acid be gruadually added to a solution of borax coloured with litmus,

the liquid will retain its purple-red colour as long as any of the borax remains undecomposed; but as soon as the last portion of the borate of soda has been converted into sulphate, the smallest additional quantity of sulphuric acid will change the purple-red to bright red. The quantity of sulphuric acid thus used gives by an easy calculation the quantity of borax contained in the liquid, each equivalent of sulphuric acid (SO = 40) corresponding to 1 eq. of soda (NaO = 31) or 1 eq. of pure crystallized borax ($NaO . 2BO^3 + 10$ Aq. = 31 + 70 + 90 = 191).

The mode of conducting the process is as follows: Dissolve 100 grains of the borax to be examined in about 1000 grain-measures of pure water, with the aid of heat, and add thereto a few drops of tincture of litmus. Then pour into an alkalimeter 1000 grain-measures of test sulphuric acid of sp. gr. 1·032 (containing 1 eq. of the anhydrous acid (SO^3), and therefore capable of neutralizing 1 eq. of soda), and add it gradually to the solution of borax till an additional drop changes the purple-red colour to bright red, indicating that the point of saturation is attained. Suppose that for this purpose 47 divisions of the alkalimeter, or 470 grain-measures of test acid have been used: then as each 1000 gr. m. of the test acid neutralize 31 grs. of soda, 470 gr. m. of the acid will neutralize $31 \times 0{\cdot}47 = 14{\cdot}57$ grs. of soda. This, therefore, is the quantity of soda contained in the sample of borax: and the quantity of crystallized borax employed is found from the proportion:

$$31 \text{ soda} : 191 \text{ borax} = 17{\cdot}7 : x = 89{\cdot}8$$

that is to say:

The sample of borax examined contains 89·8 per cent. of pure crystallized biborate of soda with 10 eq. of water.

As the accuracy of this process depends essentially on the instantaneous detection of the change of colour from purple-red to bright red, it is best to tinge a quantity of water equal to that of the borax-solution with litmus, redden it with two drops of sulphuric acid, and compare the tint of this liquor with that of the solution of borax under examination. As the boracic acid contained in the hot solution of borax is deposited when the point of saturation is attained, and interferes with the ready appreciation of the change of colour, the solution should be allowed to cool before adding the last drops of acid. When the tinge produced in the borax-liquor is exactly like that of the standard liquid, the number of divisions of the alkalimeter should be read

off. The indication is a little too high, because it is necessary to add a slight excess of the acid to produce a distinct reddening: hence it is customary to deduct three drops from the number indicated by the alkalimeter.

Borax is frequently adulterated with *common salt* and *alum*. The former may be detected by nitrate of silver, which forms a white curdy precipitate of chloride of silver, insoluble in hot nitric acid; the latter by the white bulky precipitate of alumina thrown down on adding ammonia to the solution. When the quantity of alum is considerable, its presence may also be detected by its styptic taste and acid reaction, the borax itself being slightly alkaline to test-paper.

Borate of Ammonia ($NH^4O . 2BO^3 + 4HO$) is obtained by treating boracic acid suspended in water at 50° C. (122° F.) with a slight excess of ammonia. The solution on cooling yields the salt in rhomboidal octohedrons. It might also be obtained, and more conveniently, by decomposing borax with sulphate of ammonia at the boiling heat. Sulphate of soda would then be precipitated, and the mother-liquor would yield by evaporation crystals of borate of ammonia. (Payen.)

The crystals of this salt effloresce in a dry atmosphere, giving off part of their water of crystallization. At a red heat, the whole of the water and ammonia are expelled, and boracic acid remains behind.

The solution of borate of ammonia has been successfully applied for the purpose of rendering muslin and other tissues non-inflammable. When tissues thus impregnated are held on the flame of a candle they are merely carbonized, the water and ammonia which escape preventing the communication of the flame. If the contact with the flame is prolonged, the boracic acid melts and forms a glossy varnish round the charred tissue which prevents it from taking fire. Borate of ammonia is preferable for this purpose to phosphate of ammonia or alum, the former being too costly, and the latter deteriorating the delicate tints of many tissues. (See p. 52.)

Borate of Lime.—The borates of soda and ammonia are also prepared from a native borate of lime and soda found in large quantities in Peru. This mineral, commonly called borate of lime, is known mineralogically as *Boronatrocalcite* or *Borocalcite*, *Hydroborocalcite* and *Hayesin*; also by the local name of *Tiza*.

It is found in a large plain of the Province of *Tarapaca*, called the pampa of *Tamarugal*, situate about 3300 feet above the level of the sea, and running with slight variation in a direction from North to South, from the *quebrada* of *Pisagua* to the river *Loa*, marking the division line with the republic of *Bolivia*.

This great plain is bounded by two mountain chains which run longitudinally, one rising abruptly very near the sea, the other being formed by the ramifications of the great cordillera of the *Andes*. The geological formation of these chains is very varied. In the coast line we note granites, sienites, volcanic conglomerates, &c.; in that which forms the foot of the Cordillera are to be noted alluvions, out of which rise in various places naked porphoroidal trachites. The country presents in many points a volcanic aspect, with some extinct craters having large quantities of feldspathic and ferruginous lava scattered over the surface. The masses of lava present many cavities and undulations on the surface, showing that they ran in a pasty state over a slightly inclined plain.

It appears that there once existed a large quebrada between the two chains, which has become filled with sands, clays, and fragments of rock, thus forming the large plain, which appears to have been afterwards covered by the sea, from the immense deposits of common salt that it contains.

It is in the same *pampa* and its neighbourhood that the borate of lime is found, and those large masses of salitre (nitrate of soda) are extracted which are exported to Europe. It ought to be remarked that the nitrate of soda is found only near the mountain range of the coast, and principally in formations which are slightly inclined and near volcanic formations.

The formation containing the borate of lime, as well as the salt itself, varies much, this substance being found in some parts in a loose earth, forming deposits which at times appear upon the surface, and at others at a depth of half a yard or more. In this deposit the borate of lime is found, scattered in nodules, of various size, from a grain of Indian corn to a good sized potato. The salt, in its present form, is as white as snow, fibrous in structure, with a silky appearance. In another part of the same substance, we find it beneath a very hard crust (called in the province "*caliche*"), which consists of either nitrate of soda or common salt combined with other substances.

The borate of lime beneath the crust of salitre is also found in the form of round masses, but much less numerous and almost always accompanied by crystals of glauberite (sulphate of soda and lime), a substance of no value. Lastly, the borate of lime, which is covered by the caliche, is always accompanied by a large proportion of other salts, such as chloride of sodium and sulphate of soda, which diminish its value; it is found at times in shapeless masses of a pasty consistency, but always of fibrous structure, or in hard masses, with a yellow colour externally and varying greatly in composition.

The composition of the borate of lime, as we have already said, is very variable; but to convey a more exact idea, we give the results of the analyses of the principal varieties.

Borate of lime and soda found between the establishment of the "Independencia" and the "Colombia." (Dr. Perey.)

Boracic acid (fused)	43·04	Water	27·22
Lime	14·06	Sulphuric acid	1·10
Soda	7·05	Lime	14·32
Chloride of sodium	trace	Soda	8·22
Sulphate of soda	trace	Potash	0·51
Water	35·00	Chloride of sodium	1·65
Earthy matter	0·85	Sand	0·32
	100·00		53·34
		Boracic acid and borate of soda by difference	46·66
			100·00

Sample of Borate of Lime in the "Cabreria."

Fused boracic acid	42·20
Lime	14·25
Soda	6·75
Chloride of sodium	1·60
Water	35·20
	100·00

Sample analysed by Ulex (Ann. Ch. Pharm. lxx. 51).

Boracic acid	49·50
Lime	15·70
Soda	8·80
Water	26·00
	100·00

Sample found below the Salitres of "Zapiga."		*Sample analysed by Dr. Anderson, of Glasgow.*	
Fused boracic acid . .	39·12	Boracic acid	47·25
Sulphuric acid . . .	1·45	Lime	15·98
Nitric acid.	1·60	Soda	9·88
Lime	10·06	Sulphuric acid . . .	0·45
Soda	8·22	Sand	0·98
Chloride of sodium . .	3·45	Water	25·46
Water	36·10		100·00
	100·00		

Samples of Borate of Lime. (*Richardson and Browell.*)

Boracic acid . . .	39·50	Boracic acid	20·00
Sulphuric acid . . .	2·06	Lime	11·39
Lime	12·97	Carbonate of lime .	·22
Soda	7·28	Sulphate of lime . .	15·39
Chloride of sodium . .	trace	Sulphate of soda . .	12·82
Carbonate of magnesia .	1·06	Chloride sodium . .	5·75
Insoluble matter . . .	2·50	Clay, sand, &c. . . .	11·90
Water and organic matter	33·50	Water	22·34
	98·87		99·81

Sample analysed by Lecanu (J. Pharm. [3] xxiv. 22).

Borate of lime	26·35
Borate of soda	13·44
Sulphate of soda	5·04
Chloride of sodium	9·87
Earthy residue	10·70
Water (of which 16·6 pts. go off at 100° C.) .	34·60
	100·00

	A. Dick. (*Phil. Mag.* [4] vi. 50.)	Rammelsberg. (*Pogg. Ann.* xcvii. 301.)	H. How. (*Sill. Am. J.* [2] xxiv. 230.)	
Boracic acid (anhydrous)	45·66	43·70	41·97	44·10
Lime	14·32	13·13	13·95	14·20
Soda	8·22	6·67	8·36	7·21
Potash	0·51	0·83		
Magnesia			0·04	
Water	27·22	35·67	34·39	34·49
Chloride of Sodium .	2·65			
Sulphuric acid (SO^3) .	1·10		1·29	
Sand	0·32			
	100·00	100·00	100·00	100·00

	Helvig. (*Polyt. J.* cxlvii. 218.)	Reichardt. (*Arch. Pharm.* [2] xcvi. 257.)	
Boracic acid (anhydrous) .	46·46	52·05	50·42
Lime	14·03	11·56	12·10
Soda	5·17	trace	trace
Water	32·61	34·91	34·54
Chloride of Sodium . . .	1·89		
Sulphuric acid (SO^3) . .			1·07
Chlorine		0·94	1·21
Magnesia and Silica . .	traces		
Insoluble matter . . .			0·66
	100·16	99·46	100·00

Salvétat (*Rép. Chim. appliquée*, i. 215) has analysed a borate of lime mixed with sulphate of soda and chloride of sodium, from the province of Carapaca, in Peru, containing—

Boracic acid (anhydrous) .	12·11	30·18	34·74
Lime	16·32	11·00	15·78
Water	41·25	45·50	35·00
Sulphuric acid (SO^3) . .	10·66	2·72	0·34
Soda	8·95	7·24	8·33
Chlorine	3·71	1·73	8·49
Sodium	1·50	1·13	0·32
Iodine and Bromine . .	traces	traces	traces
Earthy matter	8·00	2·60	2·90
	94·50	99·50	105·90

The preparation of boracic acid and the alkaline borates from native borate of lime or borate of magnesia has been patented by Messrs. Bell and Scholefield (1852, July 25th, No. 1633), and by W. Beatson (1855, Dec. 5th, No. 2736). Bell and Scholefield take about 500 lbs. of the mineral borate of lime in a powdered state, and boil it in as much water as will cover it, adding by degrees about 145 lbs. of oil of vitriol of commerce, and continuing the boiling for about an hour. The liquor thus obtained is then allowed to settle, and the clear liquor is drawn off—or the liquor may be filtered; the residue is to be washed, and the clear liquor mixed with the previous liquor, and in this state evaporated, the boracic acid crystallizing out. But it is better to add a saturated solution, containing about 500 lbs. of crystals of carbonate of soda (or the equivalent quantity of dry carbonate of soda) to the clear liquor, boil it for about an hour, and proceed as before. The solution thus pro-

duced is then to be evaporated till a pellicle forms, when the borate of soda is to be crystallized out in the usual way. In place of sulphuric acid being used to neutralize the alkaline and earthy matters, muriatic acid or oxalic acid in equivalent quantities may be employed, and the process conducted as above described, but it is better to use sulphuric acid, as above explained.

The mineral borate of lime may be treated directly by boiling in water with the crystals or dry carbonate of soda, as above explained, without first neutralizing by acid; but this process is not regarded by the inventors as equally advantageous with that first described.

W. Beatson prepares borate of soda and borate of ammonia from the native borate of lime and magnesia, as follows:

1. Four cwt. of borate of lime are heated in a reverberatory furnace with 2 cwt. of dry carbonate of soda, or an equivalent quantity of the same in crystals, or an equivalent quantity of sulphate, hydrochlorate, or other cheap salt of soda, the mixture being kept in the fused state and red-hot for about half an hour, and care being taken not to heat it too strongly. The mixture is then lixiviated with water, the solution evaporated, and the borax crystallized out in the usual way.

2. Ten cwt. of the mineral borate of lime or magnesia are boiled in a closed iron vessel with about 5 cwt. of sulphate of ammonia, and a sufficient quantity of water, for 2 hours, collecting in the usual way any ammonia that may be given off. The whole is then run off and allowed to settle, and the resulting sediment subjected to a similar treatment with the same quantity of sulphate of ammonia a second or third time, if found necessary. The clear liquor, consisting chiefly of borate of ammonia, may be evaporated and crystallized, and the resulting borate of ammonia employed for purposes for which borax or borate of soda is now used; or it may be converted into boracic acid by distilling off the ammonia by heating it in a closed retort. It is better, however, to add to the clear solution of borate of ammonia as much sulphuric acid as will rather more than unite with the ammonia, evaporate the solution, and crystallize out the boracic acid, the resulting liquor, containing principally the sulphate of ammonia, being again employed for a fresh operation on a further quantity of the mineral borate of lime or magnesia.

3. Ten cwt. borate of lime or magnesia, and a similar quantity of sulphate of soda, with ½ cwt. of sulphate of ammonia, are

boiled together with about 200 gallons of water for 5 or 6 hours, the mixture being allowed to settle, and the clear liquor evaporated and crystallized in the usual way; or, better, boiled again for a similar time in about 10 cwt. of a fresh quantity of borate of lime or magnesia, after which the borax may be crystallized out.

4. For many purposes for which borax is employed, it is not necessary to separate the lime, &c., from the boracic acid with which it is combined in the mineral borates of lime and magnesia. It is sufficient, therefore, to take the mineral as imported, and subject it to such cleaning process, by picking and washing, as may be necessary, and, by preference, mix it with dry carbonate of soda, by grinding both together to a fine powder in various relative proportions. The same object may be effected by mixing the mineral borate of lime, as aforesaid, with potash, silica, alumina, oxide of lead, or other alkaline or earthy ingredients which are used as glazes for pottery, &c., or for other purposes for which borax is employed.

Dr. Richardson, of Newcastle, uses native borate of lime, after purification, as a substitute for borax in the manufacture of glass and also of frits for clay-wares, thereby saving the expense of converting the borate of lime into borate of soda (patented 1855, Oct. 23rd, No. 2371).

To free the borate of lime from the soluble impurities, chlorides, sulphates, &c., which the mineral as imported into this country contains, it is levigated in a manner similar to that in practice in colour-works, "a small jet of steam being admitted into the dolly tub to promote the purification. The sand and coarser impurities are separated in the dolly, while the finely divided borate of lime flows on through the spouts into tanks, where it subsides, leaving the soluble impurities in solution in the supernatant liquid, which may be syphoned or run off. The borate of lime is dried in dishes in stoves, or in reverberatory furnaces, with a gentle surface-heat, and occasional agitation by the workman. For coarser wares and inferior qualities of glass it is unnecessary to carry the purification to such an extent. The adhering sand and other impurities may be removed by simply brushing off the sand or impurities from the masses, or exposing them to a current of water.

"The purified borate of lime in powder may be employed as a substitute for borax in the manufacture of frits for clay-wares; in the impure state it injures the colour of the ware.

"For every 100 parts of borax, a quantity of borate of lime, containing a like quantity of boracic acid, should be used in preparing a frit, with borate of lime in place of borax. Or the purified borate of lime is mixed with a quantity of soda, which it is best to use in the form of carbonate, in the proportion of one part of the latter to four parts of the former, exposed to a gentle heat in a close furnace. The resulting material may be used to replace the equivalent quantities of borax and whiting in the frits or glazes employed in manufactories of clay-wares. The above proportions produce a transparent glaze or glass, but where that is not desired it is better to employ more soda. The workman will readily ascertain when the above process is completed, by taking a small quantity of the mixture from the furnace and tasting it when cool, and if he finds that it offers a sweetness to the taste, and not an alkaline flavour, the preparation is complete.

"In the manufacture of glass, the purified borate of lime is used as a substitute for borax in such proportion that the quantity of boracic acid always remains the same in the manufacture of flint, plate, crown, and sheet glass; but the crude borate as imported, reduced to powder, is sufficiently pure for pale glass, such as is employed in making medicinal bottles and other like descriptions of glass. In such application, where lime and soda are usually employed as constituents of the glass, it is unnecessary to resort to the preliminary process of fritting; and, if preferred, sulphate of soda may be substituted for the carbonate, in the proportion of 72 of the former for 54 of the latter, where phosphate of soda has heretofore been used in the manufacture of glass. In such cases the patentee does not recommend the use of borate of lime."

SOLUBLE PHOSPHATES.

THE salts of this class are arranged in three groups, corresponding to the three hydrates of phosphoric acid, and having a composition represented by the following formulæ:—

Monobasic phosphates, or metaphosphates . .	$MO.PO^5$
Bibasic phosphates, or pyrophosphates . . .	$2MO.PO^5$
Tribasic phosphates	$3MO.PO^5$

The quantity of a fixed base with which phosphoric acid com-

bines is thus exactly equivalent to the proportion of water in the hydrated acid.

In addition to the above salts, recent investigations have established the existence of several intermediate classes, the interest of which is, however, purely theoretical.

The alkaline phosphates of all these classes are soluble; the tribasic phosphates of the earths, and most of the phosphates of the metals, are insoluble in water, but soluble in excess of phosphoric acid and in all the strong mineral acids; the phosphates of lime and magnesia are soluble also in acetic acid.

It is to the *soluble* phosphates that attention is here particularly directed, as being those which find practical applications in medicine and in agriculture.

Phosphate of soda, tribasic phosphate, $HO.2NaO.PO^5 + 24Aq.$, is the salt known in pharmacy as a mild saline cathartic; and as a purgative employed in affections of children, being recommended especially by its absence of nauseous taste and its gentle action. It is prepared on a scale of some magnitude by treating finely powdered bone-ash with four-fifths of its weight of sulphuric acid diluted to four or five times its bulk with water, neutralising with carbonate of soda till a slightly alkaline reaction is produced, boiling, filtering from insoluble phosphate of lime, and crystallizing, care being always taken to maintain the slightly alkaline reaction of the liquors. The precipitated insoluble phosphate of lime may be dissolved in nitric acid, sulphate of soda added, and the nitric acid distilled off. The residue is treated with water, and the liquors crystallized.

This salt crystallizes in oblique rhombic prisms, which are efflorescent on the surface; it is soluble in four parts of water at 60° Fah., in two parts at 212°, and fuses at a low red heat in its own water of crystallization, which at a higher degree passes off.

There are two other tribasic phosphates of soda containing respectively $3NaO.PO^5 + 2Aq.$, and $2HO.NaO.PO^5 + 2Aq.$

The former, *subphosphate of soda*, is formed by adding caustic soda in excess to solution of the ordinary phosphate. It is a crystallizable salt, soluble in five parts of water at 60° F., and melting in its own water of crystallization at 170°. It is highly unstable, being decomposed by the weakest acids, even by carbonic acid, which abstract one third of its alkaline base.

The latter salt, *biphosphate of soda*, is formed by adding terhydrated phosphoric acid to the ordinary phosphate, until the

solution ceases to precipitate chloride of barium. It is a highly soluble salt, of acid reaction, crystallizing with difficulty in right rhombic prisms of two modifications.

Dr. Clark first observed that, at a red heat, ordinary tribasic phosphate of soda is decomposed, losing not only its water of crystallization, but also its basic water. The residue is the new salt, the *bibasic phosphate*, or *pyrophosphate*, which is less soluble than the tribasic salt, and separates in prismatic crystals, containing ten equivalents of water, and represented by $2NaO . PO^5 + 10Aq$.

The corresponding salts of potash and ammonia cannot be obtained in the solid form, as they reassume their basic water in crystallizing, being converted into the original tribasic salts. When the biphosphate, $2HO . NaO . PO^5 + 2HO$, *i. e.*, the tribasic phosphate with only one equivalent of fixed base, is heated to redness, it parts with the whole of its water, basic as well as that of crystallization, and the residue constitutes *metaphosphate of soda* of the formula $NaO . PO^5$. The fused mass forms on cooling a transparent glass, highly deliquescent, of feeble acid reaction. The solution does not crystallize, but evaporates to a gummy mass, containing approximately one equivalent of water. The *metaphosphate of soda* can be obtained in the crystalline form only by extremely slow cooling of the fused salt.

The metaphosphates of magnesia, nickel, copper, lime, baryta, and alumina, have been obtained. They are all insoluble in water, and of no practical interest.

Phosphate of Soda and Ammonia, or *Microcosmic Salt*, $HO . NH^4O . NaO . PO^5 + 8Aq.$, is a salt much employed in laboratory operations as a flux, being, in fact, a ready source of metaphosphate of soda, into which it passes on the application of heat, losing first its eight equivalents of water of crystallization, and at a stronger heat its remaining water and ammonia.

It is prepared by mixing 2 parts water, 1 part chloride ammonium, and 7 parts of crystallized phosphate of soda of commerce. Chloride of sodium is deposited in granular crystals, and the solution, filtered off and concentrated, yields prismatic crystals of the above salt, which are purified by recrystallization from adhering chloride of sodium.

The corresponding salt, containing potash instead of soda, has not been obtained.

Phosphate of Magnesia and Ammonia is a tribasic salt,

having 1 eq. of ammonia, and 2 eq. of magnesia, and 12 eq. of water, of which 10 may be expelled without further alteration of the salt. Its formula is $NH^4O . 2MgO . PO^5 + 2HO + 10Aq.$ It is soluble in pure water, readily dissolved by all acids, but quite insoluble in water containing saline matters or ammonia. At a high temperature, it loses its ammonia and water, and becomes pyrophosphate of magnesia. Its chief interest is that it constitutes the granular precipitate which falls on mixing solutions of tribasic phosphates, in presence of ammonia, with magnesia salts, by the formation of which both magnesia and phosphoric acid are estimated in analysis. It forms also the chief constituent of a particular form of urinary calculus. The corresponding salts, containing 2 eq. of lime, baryta, strontia, and one in which the ammonia is replaced by potash, have been formed.

Phosphates of Lime.

Metaphosphates and pyrophosphates of lime exist analogous to the soda-salts, but it is the ordinary triphosphate which claims attention as a substance of the utmost importance in the arts and in agriculture.

It occurs naturally, in combination with chloride or fluoride of calcium, in apatite and moroxite, $CaF . 3 (CaO . PO^5)$, and, mixed with carbonate of lime and traces of fluoride of calcium, constitutes the chief part of the ashes of bones. It may be separated from bones by dissolving them in hydrochloric acid and precipitating by ammonia, when it is obtained as a bulky gelatinous deposit, caking together into a hard mass of conchoïdal fracture when dried, and fusing at a very high temperature—estimated by Saussure at 378° Wedgewood—into a substance resembling porcelain. Berzelius, however, considers this precipitate to consist of $8CaO . 3PO^5$, and concludes that the composition of bone earth is variable.

Triphosphate of lime, of the formula $3CaO . PO$, is also precipitated by adding excess of an alkaline diphosphate to a solution of chloride of calcium.

$$3\,CaCl + 2(2MO . PO^5) = 3CaO . PO^5 + 3MCl + MO . PO^5.$$

Diphosphate of lime is precipitated on adding solution of diphosphate of soda to an excess of chloride of calcium, or when a solution of chloride of calcium is precipitated by a slight excess of ordinary phosphate of soda, the solution divided into two equal parts, together with the suspended precipitate, one half dissolved

up with the smallest possible quantity of hydrochloric acid, and the other portion then added. After the lapse of 48 hours, the precipitate presents the appearance of thin tabular rhombic prisms of the formula $2CaO.HO.PO^5 + 4Aq$. (Gmelin.)

The *Monophosphate* consists of small crystalline scales of acid taste and deliquescent. It is formed when a solution of triphosphate or diphosphate in phosphoric, nitric, or hydrochloric acid is evaporated slowly to the crystallizing point. If 155 parts of bone-ash are digested with from 100 to 150 parts of oil of vitriol suitably diluted, abundance of sulphate of lime is formed, and the liquid contains free phosphoric acid and the monophosphate in variable proportions. This solution, upon evaporation and fusion, gives a transparent acid glass, constituting the *superphosphate*. It is a solution of the kind above described, absorbed or dried up by various other substances, which forms the *superphosphate of lime* of commerce, now prepared on an enormous scale as a manure.

The importance of a supply of phosphates to the land is evident from the consideration that the soluble parts of blood-ash are chloride of sodium and *alkaline phosphates*, the insoluble consisting of phosphates of lime and of magnesia, and oxide of iron, which substances must be ultimately, either directly or indirectly, derived from vegetables. Accordingly, scarcely any plants are devoid of phosphates as one of their essential elements, while those parts of them are the most nutritious, which contain the largest portion of these salts, such as seeds and grain, more especially the several varieties of bread-stuffs, peas, beans, and lentils. Consequently no seed suitable to become animal food can be grown without the presence of phosphates; and for the production of the largest crop, the soil must contain a preponderating proportion of the food necessary for the formation of seeds.

It is necessary, furthermore, to bear in mind the enormous amount of mineral matter annually extracted from the soil in the shape of vegetable and animal food, of bread, beef, and mutton, for the supply of the dense population of our cities and *not returned*. These matters are collected by a huge and complex system of supply from a vast acreage of ground, and the greater part of them is lost in the form of fluid and solid excreta, representing on an average 10,300,000 lbs. of mineral substances per annum per each million of inhabitants, mostly the ash-constituents of bread and meat.

The following Table (taken from Johnston's Lectures on Agricultural Chemistry, 2nd ed., 1847, p. 414,) exhibits the relative quantities of mineral ingredients in the ash of various plants cultivated for food:

	Potash and Soda.	Lime.	Magnesia.	Phosphoric acid.	Sulphuric acid.	Silica.
Wheat	33	3	12	50	0·25	1
Barley	22	3	7	39	0·10	27
Oats	26	6	10	44	11	3
Rye	34	5	10	50	1	0·4
Indian Corn	33	1	16	45	3	1
Rice	30	1	12	53		3
Beans	44	6	8	38	1	1
Peas	44	5	8	33	4	0·51
Wheat-straw	13	7	4	3	6	65
Barley do.	7	10	3	3	2	77
Oat do.	29	8	4	3	3	48
Rye do.	18	9	2	4	1	65
Maize do.	35	8	7	17		28
Rice do.	14		5	1	4	74
Bean do.	55	20	7	7	1	7
Pea do.	5	55	7	5	7	20
Red Clover	36	33	8	8	3	7
Potatoes	57	2	5	13	14	4
Turnips	47	14	5	8	14	8
Beets	56	9	5	8	2	10
Cabbage	32	21	6	12	22	0·74
Potato tops	44	17	7	8	7	4
Turnip do.	34	23	3	9	13	1

If now we assume that the four-course rotation yields 25 bushels of wheat, 40 bushels of barley, 20 tons of turnips, with 6⅓ tons of tops, and 1½ tons of hay, then the quantities given in the following Table (Johnston, *loc. cit.*, p. 409) show the pounds weight of each mineral substance removed from the soil per acre:

	Grain.	Straw.	Bulbs.	Tops.	Hay.	Total.
Potash	14·39	32·73	142·66	88·82	38·22	316·82
Soda	7·05	1·21	17·31	16·76	12·05	54·38
Lime	2·24	27·62	46·24	72·14	44·45	192·69
Magnesia	7·60	12·14	18·16	9·58	7·09	54·57
Oxide of iron with a little oxide of manganese and alumina	1·11	5·96	4·35	2·67	0·58	14·67
Phosphoric acid	35·76	10·56	25·77	28·80	15·12	116·01
Sulphuric acid	0·12	13·15	46·24	38·81	9·20	107·52
Chlorine	0·02	3·55	12·24	49·75	4·06	69·62
Silica	14·71	233·08	27·03	2·67	78·23	355·72
	83·00	340·00	340·00	310·00	209·00	1282·00

To replace by art the inorganic ingredients carried off in this rotation, a mixture of saline substances must be returned to the soil every four years in the following proportions:

Dry pearlash	465 lbs.
Ordinary bone-bust . . .	552
Epsom salts	326
Common salt	116
Quicklime	70
	1529

To give an idea of the natural capabilities of soils for supplying mineral food to plants, we subjoin the following analyses made by various chemists:

	Rich vegetable mould.	Good sandy soil.	Good clayey soil.	Good loamy soil.	Lime soil	Marly soil.	Fertile alluvial soil.	Moorland soil.	Sandy soil.	Indifferent soil.
Organic matter, humus, &c. ..	10·08	·49	3·38	11·24	6·33	10·50	4·76	28·11	1·50	·85
Oxide iron ..	6·30	3·19	8·82	4·87	9·31	11·92*	2·40†	·25	2·00	2·49
Alumina ..	9·30	2·65	6·67	14·04			·45 6·43	1·05	·51	·10
Lime	1·01	·24	1·44	·83	54·56†	19·92	·74	trace	trace	·04
Magnesia	·20	·70	·92	1·02	trace	·25	·53	·01	do.	·15
Potash	·01	·12	1·48	2·80	1·03	·71	·01	trace	do.	·09
Soda		·02	1·08	1·43						
Phosphoric acid..	·13	·07	1·51	·24	trace	·38	·12	do.	do.	·16
Sulphuric acid ..	·17	traces		·09	do.	·04	·46	do.	do.	·01
Chlorine		do.		·25	do.	·76	trace	do.	do.	·01
Insoluble silicates	72·80	92·52	72·83	63·19	28·77	55·52	84·51	70·58	96·00	95·70

"In 1848 the Royal Institute of Rural Economy, in Berlin, caused the soil from 14 different places of the kingdom to be submitted to chemical analysis. It resulted from these analyses that the mean quantity of phosphoric acid and potash (the latter in a state probably fit for assimilation) amounted in 5 fields to ·2; in 6 to ·3 up to ·5; and in 3 to ·5 up to ·6 per cent."—Liebig, Modern Agriculture, p. 143.—See also page 226.

The substances chiefly used for supplying phosphoric acid to the soil are bones, bone-ash, native phosphate of lime, in the form of apatite, osteolite, phosphorite, coprolites, &c., and superphosphate of lime, prepared by treating the several substances with sulphuric acid. The following are analyses of various natural substances containing phosphoric acid:

* Oxide of Manganese. † Carbonate of lime.

1. *Bones* may be stated to be composed as follows:

Cartilage, fat, water, &c. . . .	48
Phosphate of lime, magnesia . .	46
Carbonate of lime	4
Alkaline chlorides, and sulphates .	2
	100

2. *Bone-ashes* vary very much in composition, and the following analyses are selected as representing fair cargoes:

	Anderson.			Richardson.			
Water	6·10	6·28	3·03	10·90	3·80	15·00	1·80
Charcoal . . .	5·05	2·19	2·02	2·01	3·35	trace	4·35
Phosphates . .	79·20	71·10	88·55	80·05	80·10	73·51	82·55
Carbonate of lime	4·05	3·55	5·60	3·50	6·41	4·31	5·18
Alkaline salts .	·15	trace					
Sand, &c. .	5·45	16·90	·80	3·54	6·34	10·18	6·12
	100·00	100·00	100·00	100·00	100·00	100·00	100·00

3. *Bone-black*:—No. 1. From the sugar refineries. Fine matter collected on the filters, and having been used for clarification with blood or white of egg. Applicable to soils poor in organic matter.

No. 2. Substance generally granular, having undergone a considerable number of revivifications. Applicable to soils rich in organic matter.

The analyses give the quantities of the several constituents in 1000 parts.

	No. 1. Refinery of Nantes.		No. 2. Russia.	New York.
Nitrogen	30·0	25 0	9·2	7·9
Charcoal (organic matter) .	38·0	31·0	17·5	5·5
Soluble salts	1·3	1·2	0·5	0·4
Phosphate of lime	54·0	60·0	68·5	81·0
Carbonate of lime	3·0	4·0	7·0	9·0
Silica	2·0	3·0	5·0	3·0
Magnesia	0·9	0·8	1·5	1·1

4. Native phosphate of lime, which occurs in hexagonal crystals as *Apatite*, in radiated masses as *Phosphorite*, and in the earthy form as *Osteolite*, is largely imported into this country as a manure. Apatite and phosphorite contain fluoride and chloride of calcium associated with the phosphate; in osteolite, which

appears to be an altered product, the chlorine and fluorine have disappeared. *Coprolites*, which consist chiefly of the fossil excrements of extinct animals, and contain a large proportion of phosphate of lime, are also much used in the preparation of artificial manure. The following are analyses of these substances:

Apatite ($3CaO.PO^5$) + $\frac{1}{3}$ CaF.

	Rammelsberg.[1] Schwarzenstein.	Weber.[2] Snarum.	Joy.[3] Faldigl.	Henry.[4] Huel Franco.
Phosphoric acid	42·58	41·54	43·01	41·34
Lime	49·66	53·46	55·24	53·38
Calcium	4·06	—	—	—
Chlorine	0·07	2·66	0·05	—
Fluorine	3·63	?	?	—
Sesquioxide of iron	—	1·79	0·09	—
Sesquioxide of Cerium	—		—	—
Yttria	—		—	—
Protoxide of iron	—	—	—	2·96
Protoxide of manganese	—	—	—	
Loss	—	—	—	2·32
	100·00	99·45	98·39	100·00

	J. D. Whitney.[5] Hardstown, New York.		G. Rush.[6] Minsk, Siberia.		Damour.[7] Ariège, Pyrenees.	
Phosphoric acid	43·28	43·17	42·08	42·08	40·00	
Lime	53·50	53·37	55·17	49·75	47·31	
Calcium	—	—	—	3·87	3·60	
Chlorine		1·02				
Fluorine	trace	trace		3·97	3·36	
Sesquioxide of iron			0·17	0·17	0·43	($Fe^2O^3.PO^1$)
Water			0·16	0·16	5·30	
Organic matter						
Insoluble substance	0·29	0·25				
	96·98	97·79	97·58	100·00	100·00	

	G. Rose (Pogg. ix. Dana ii. 397). Snarum, Norway.	Cabo de Gata, Spain.	Arendal, Norway.	Greiner, Tyrol.	St. Gothard, Tyrol.
Phosphate of lime	91·13	92·066	92·189	92·16	92·31
Chloride of calcium	4·28	0·885	0·801	0·15	trace
Fluoride of calcium	4·59	7·049	7·01	7·69	7·69
	100·00	100·000	100·000	100·00	100·00

(1) Mineralchemie, s. 353. (2) Monatsber. Preuss. Akad. 1851, 173.
(3) Dana. Miner. ii. 397. (4) Ibid. 397; Phil. Mag. [3] xxxvi. 134.
(5) Sill. Am. J. [2] xvii. 209. (6) Pogg. Ann. xcvi. 331.
(7) Ann. Min, [5] x. 65. A hydro-apatite, $3CaO.PO^5 + \frac{1}{3}$ CaF. + HO.

Apatite from Krageroé, in Norway, analysed by VÖLCKER (Reports of the British Association, 1857, p. 59).

	Red.		White.	
Phosphoric acid	41·88	41·74	41·25	42·28
Lime	53·45	54·12	50·62	53·35
Chloride of calcium	1·61	1·61	6·41	2·16
Magnesia		0·20		
Alumina			0·38	0·92
Sesquioxide of iron			0·29	
Phosphates of iron and Alumina	1·66	0·45		
Insoluble water	1·24	0·97	0·82	0·99
Water { hygroscopic	0·43	0·43	0·19	0·30
Water { chemically combined	0·40	0·40	0·23	0·20
Alkalies		0·30	0·17	
	100·67	100·22	100·36	100·20

Considerable quantities of apatite are now imported from Spain. Anderson found in a sample from this source:

	Anderson.
Water	·80
Phosphate of lime	93·30
Carbonate of lime	·50
Chlorine	trace
Sand	4·70
	99·30

Osteolite.

	BROMEIS.(1) From Hanau, between Ostheim and Eichen.			RÜTZ.(1) EWALD.(1) SCHRÖDER.(2) Amberg, in the Harz.	DÜRRE.(3) Kratzenberg, in Bohemia.
	Compact.	Earthy.	Intermediate.		
Phosphoric acid	36·88	37·41	37·16	42·00	34·64
Lime	49·41	49·24	48·20	48·16	44·76
Silica	4·50	2·75	2·03	4·97	8·89
Sesquioxide of iron	1·85	2·78	2·31	1·56	0·51
Alumina	0·93	1·25	trace	—	6·14
Magnesia	0·47	0·79	1·85	0·75	0·79
Potash	0·76	0·81	0·73	0·04	—
Soda	0·62	0·46	0·43	0·02	—
Carbonic acid	1·81	2·34	2·55	2·21	—
Water	2·28	3·45	3·63	1·31	2·97
Chlorine	—	—	—	—	trace
	99·51	101·28	98·89	101·02	98·70

(1) Ann. Ch. Pharm. lxxix. 1. (2) Ibid. lxxxix. 221.
(3) Pogg. Ann. cv. 155.

In *phosphorite* from Hounef, near Bonn, Bluhme found 37·33 PO^5, 47·50 CaO, 3·50 SiO^3, 3·28 Al^2O^3, 2·70 MgO, 2·20 CO^2, 1·65 water, and a trace of chlorine. (Ann. Ch Pharm. xciv. 354.)

Coprolites.

	T. J. Herapath. (1) From the Coast of Suffolk.				T. S. Hunt. (2) From the Lower Silurian Strata of Canada.			Dana. (3) From Sandstone in the Connecticut Valley.	Reuss (4) From Bituminous Shale in Bohemia.	Wolff. (5) From Rothenburg, on the Tauber.	Hassenkamp. (6) From Lignite, near Roth, in the Rhongebirg.	Meugy. (7) From the Chalk near Rethel, in France.
Phosphoric acid	—	—	—	—	—	—	—	—	24·43	—	—	21·29
Phosphate of lime 3 CaO·PO^5	70·9	15·86	60·8	67·53	40·34	36·38	44·70	} 39·60	—	55·8	45·58	—
Phosphate of magnesia 3 MgO·PO^5	trace	—	—	—	—	—	—		—	—	—	—
Phosphate of alumina	1·6	4·71	—	—	..	—	—		—	—	—	—
Ferric phosphate ..	6·9	9·2	4·1	—	—	—	—	—	—	—	2·04	—
Fluoride of calcium ..	0·61	1·7	—	—	—	—	—	—	—	—	27·71	—
Carbonic acid	—	—	—	—	—	—	—	—	—	—	—	—
Carbonate of lime ..	10·28	39·5	23·7	4·35	5·14	5·00	6·60	34·77	13·29	—	7·68	17·50
Carbonate of magnesia	trace	0·5	—	1·65	9·70	} 7·02	{ 4·76	—	—	—	—	—
Protoxide of iron ..	—	—	—	2·95	12·62		{ 8·60	—	—	4·5	—	—
Lime	—	—	—	—	—	—	—	—	—	—	—	—
Magnesia	—	—	—	—	—	—	—	—	49·70	—	4·20	50·50
Sesquioxide of iron ..	—	—	2·0	—	—	—	—	—	5·03	} 8·0	1·34	3·20
Alumina	—	6·2	—	—	—	—	—	—	—		0·62	—
Sesquioxide of manganese	trace	—	—	—	—	—	—	—	—	—	—	4·80
Silica	5·79	10·6	1·6	—	[2]5·44	49·90	27·90	—	—	9·7	—	—
Sand	—	—	—	21·10				13·10	—	13·7	—	—
Sulphate of lime ..	trace	—	1·8	—	—	—	—	1·75	—	—	—	—
Sulphate of potash ..	—	—	—	—	—	—	—	—	—	5·8	—	—
Chloride of sodium ..	—	—	—	—	—	—	—	0·50	7·55	—	—	—
Soluble salts	traces	traces	traces	—	—	—	—	—	—	—	—	—
Water	4·00	11·60	6·1	2·15	2·13	1·7	5·00	7·30	—	—	7·50	1·00
Organic matter												
Urate of ammonia and lime	—	—	—	—	—	—	—	3·00	—	—	3·33	—
	100·08	99·47	100 1	99·73	95·37	100·00	97·56	100·02	100·00	98·5	100·00	98·29

The chalk marl and adjoining strata are very rich in petrifactions containing phosphoric acid, as shown by the following analyses made by Messrs. J. M. Paine and J. T. Way (Journ. of the Roy. Agr. Soc., vol. ix. pt. 1):

A. The *Chalk Marl*, very fertile, and containing a large quantity of phosphoric acid. B. Petrifactions on the upper marly layer of the Upper Greensand. C. Soft amorphous bodies in the same. D. The Marl itself. E. Petrifactions in the *Gault*, very rich in phosphoric acid. F. Petrifactions at the junction of of the Gault with the Lower Greensand. G. A conglomerate of petrifraction with Sandstone cement, 3 to 18 inches thick. H. Green granules from the Lower Greensand.

(1) Ann. Ch. Pharm. lxxix. 1.
(2) Pogg. Ann. cv. 155.
(3) Sill. Am. J. [2] xv. 129.
(4) Wien. Akad. Ber. xviii. 124.
(5) Jahrb. Miner. 1836, 422.
(6) Ibid. lxxxix. 221.
(7) Chem. Gaz. 1849, 449.
(8) Jab. Miner. 1847, 729.
(9) Dingl. pol. J. cxlii. 320.
(10) Compl. rend. xliii. 755.

	Insol. Silicate.	SiO^2 soluble.	PO^5	CO^2	CaO.	MgO.	Fe^2O^3.	Al^2O^3.	KO.	NaO.	Water, Organic Matter, HF, and loss.	SO^3.	Sum.
A	19·64	6·45	1·82	28·98	37·71	0·68	3·04		..	..	..	..	98·32
B (1)	7·68		29·87	8·77	42·29	..	6·87		..	..	4·52	..	100·00
C	7·18	3·28	27·13	8·77	39·85	0·96	10·60		..	..	2·49	..	100·26
D (2)	32·81	29·14	6·61	2·61	9·53	1·97	11·46		3·10	..	3·02	..	99·94
D (3)	26·83	26·30	9·31	2·35	15·24	1·43	13·11		..	..	2·64	..	97·21
G (7)	39·59	18·42	6·89	4·52	9·11	1·64	13·55		..	..	4·12	..	97·84
D (4)	7·12	3.27	33·03	5·58	46·50	trace	1·96		..	..	3·04	..	100·50
D (5)	0·91	..	24·28	12·43	47·46	0·21	2·91	..	..	..	11·80	..	100·00
E	75·46	8·12	0·64	5·64	2·01	0·18	5·59		..	..	2·30	..	99·94
F (6)	43·87	3·25	20·80	1·06*	23·86	0·37	3·35		..	..	3·44	..	100·00
H	18·58		20·65	4·01	34·61	..	7·24	0·98	1·79	1·87	2·28	5·13	97·09

* CaO . CO^2

The value of bones as a manure has long been known, their effects as a durable fertilizer of permanent grass lands having attracted particular attention; but superphosphate or soluble phosphate possesses, for most crops, the greatest advantages in superior rapidity of action and corresponding saving of capital.

It is well known that plants withdraw food only from the particles of soil in actual contact with their rootlets. Plant-food is not conveyed through the pores of the soil by rain water; on the contrary, if rain water containing ammonia, potash, phosphoric acid or silicates, be filtered through soil, these substances are wholly removed by it. Hence, there is no danger of the removal of soluble manures by periods of heavy rain, or other similar causes.

Phosphate of lime (bone earth) is slightly soluble in water impregnated with carbonic acid, as well as in solutions of ammoniacal salts, nitrate of soda, and common salt, and these substances act upon raw bones pretty much in proportion to their state of division, 50 lbs. of bone-dust being frequently equal in effect to 200 or 300 lbs. of half-inch or coarsely crushed bones, simply because the latter require more time to become *soluble*. Hence,

(1) An arborescent Alcyonites. It contains also a large quantity of amorphous spongy bodies, weighing 8 to 10 lbs., containing 5 to 50 per cent. of phosphate of lime, the quantity increasing from without inwards.

(2) Sifted marl, from which the petrifactions have been separated.

(3) Indurated marl and small fossils, which remained on the sieve.

(4) Marl from Bentley with the fossils.

(5) The fossils therefrom.

(6) After comminution and removal of the principal petrifactions.

(7) The petrifactions.

the great advantage, in economy of time and capital, derived from the use of bones rendered soluble by sulphuric acid.

Thus, in a series of experiments by Professor Voelcker, land yielding, when unmanured, 5 tons 4 cwt. of roots, gave for the expenditure of £2 in superphosphates an increase of 8 tons 8 cwt., while the same value of bone-dust gave only 3 tons 12 cwt.

Manufacture of Superphosphate.—Commercial superphosphate of lime is manufactured on an immense scale by acting on ground bones, bone-ash, coprolites, or apatite, by sulphuric acid. The former are preferable from the facility with which the acid reacts upon their porous structure, the "mineral phosphates" as the latter substances are commonly termed in contradistinction, requiring to be ground to an almost impalpable powder,* and to be subjected to a more protracted digestion, assisted by steam heat. The larger proportion of carbonate of lime which they contain also requires a larger quantity of vitriol, while, of course, a correspondingly larger amount of sulphate of lime is produced. A very convenient method of finding the exact quantity of acid necessary, is to multiply each per cent. of carbonate of lime by ·8, and each per cent. of phosphate of lime by ·52, the total representing dry sulphuric acid, which can be converted into acid of any strength by reference to the table in the appendix.

The digestion is effected in large vats, either lined with lead or constructed of compact bricks set in cement, which are found perfectly to resist the action of the acid. The bones, coprolites, or other materials are first introduced, and somewhat more than one half their weight of "brown oil of vitriol" diluted with twice its weight of water, is then poured on by degrees, the whole mass being constantly stirred up either by the aid of suitable machinery or by hand, to promote the intermixture of the materials, and steam blown in, if necessary.

Abundant effervescence and the rising of heavy vapours indicate the decomposition of the carbonates, and when this has subsided, the whole mass is left to digest for 24 hours; when, if a proper mixture has been effected, and the materials were in a state of sufficiently minute division, very little phosphate will be found to remain in an insoluble state.

The contents of the vat are now in a pasty condition from the

* A diagram of a mill for grinding phosphates is given in the article Phosphorus, p. 112.

sulphate and soluble phosphate of lime, which have been formed during the process, and from excess of water in the sulphuric acid. Various "dryers" are therefore added to absorb the superfluous liquid, such as raw bones, coprolites, ashes, sawdust, soot, or other materials procurable by the manufacturer.

Finally the "superphosphate" is removed from the vat, and dried, or if space permits stacked and allowed to desiccate by the heat which is spontaneously generated in the mass. It is then passed through sieving apparatus, and the larger masses are crushed down till the whole is reduced to a coarse powder, in which state it is fit for the market.

A machine for this purpose has lately been invented by Messrs. Richmond and Chandler, of Salford. It consists of a series of four strong cylindrical iron cages, of various sizes, concentrically arranged one within another, on a horizontal axle, on which they are caused to revolve with great velocity in contrary directions to each other, by means of open and crossed straps, the alternate cages being so arranged to intersect one another, that while, in reality, there are only two motions, there are relatively four—the first and third cages going to the right, the second and fourth to the left.

Its *modus operandi* is as follows:—The conglomerated clods of phosphate, &c., in their rough, lumpy condition, are shovelled through a central opening into the innermost cage, and are instantly delivered in a radiating shower from every part of the periphery of the outermost one into an external casing or hood, in a state of the finest granulated powder, almost if not quite as regular and uniform in grain as gunpowder. This granulating, or pulverising, is effected in the following manner:—The centrifugal action of the machine drives the material from the centre to the periphery of the outermost cage; but, before it can reach and escape from there, every grain of it meets with and receives four distinct cutting blows, delivered with great rapidity and violence, by the numerous (156) but open set bars of the intersecting cages that it encounters on its way, each of which blows is doubled in intensity by the four reverse actions of the several cages. A stout knife is fixed to a pillar cast in a piece with the carrying frame in such a manner that its blade extends into the interior of the innermost cage, which instantly arrests and cuts such pieces as are otherwise too large to pass between its bars. Immediately this first cage is passed, any unfibrous substance, if

less tenaciously pasty than dough, or not much tougher than oilcake, or any brittle material, such as silicate of soda, is, in less than a second, thrashed, cut, and beaten to pieces, and the whole of it driven out with great force from the periphery in the fine granulated powder before spoken of; which can be made either finer or coarser, by increasing or diminishing the rotating speed; for the pulverising powers of the machine are in direct proportion to its speed.

When from 20 to 30 tons a day of such a material as phosphate is to be operated on, it takes from five to six horse power to drive it at its proper speed of about 350 revolutions per minute (which, owing to the reverse actions, is equal in effect, as regards each of the four series of blows, to what would be attained at a speed of 700 revolutions). When so applied, it has been found to reduce to powder as much phosphate in a day as three men could properly do in a week with the ordinary plan of hand-screening, and in a much more efficient manner.

FIG. 99.

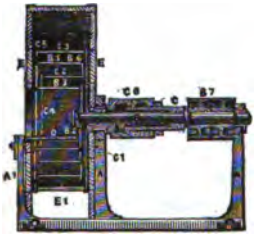


FIG. 100.

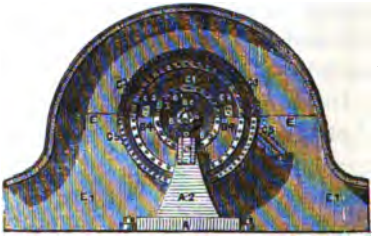


Fig. 99 is a longitudinal elevation in section, in which all the bars forming each cage, except the two in each cage which occur at the sectional line of the drawing, are omitted to avoid confusion. Fig. 100 is an end elevation of the machine, one half of the outer end disc being supposed broken away to show the cages more distinctly, the casting being also shown in section. The machine consists of a frame or headstock A, which can be bolted down to a suitable bed of stone or wood by bolts passing through the ears A1. This headstock A forms the bearing of a solid shaft B and a hollow boss or shaft C. The solid shaft, as will be seen, is conical at the end, and carries a disc plate B1, which is firmly secured to it by a key B2 passing through a slot in the end of the shaft B, as shown. This disc plate (B1) carries a series of bars (B3), which are rivetted in it at one end, and at the other end in another disc B4, in which one end of another series of bars B5 is

secured, the other end of these bars being connected together in a ring B6; thus two circular cages formed by the series of bars B3 and B5 are obtained, which will rotate with the shaft B. The hollow boss C working loose on the shaft B is solid, with the disc or face plate C1 which carries the series of bars C2 and C3, forming the cages intermediate and alternate with the cages formed by the bars B3 and B5, and the outer ends of the bars C2 and C3 are respectively connected and secured in the rings C4 and C5. The shaft B and hollow boss C are rotated in opposite directions by belts (one of them being crossed and the other open) working on the fast and loose driving pulleys B7 and C6. The hollow boss C is lubricated by passing the lubricating matter through holes formed in it, which are closed by screw plugs to prevent the lubricating matter from being thrown out when at work by centrifugal action. It will be seen that a standard A2 from the headstock or frame A carries a bar or knife D, the object of which is to break up such lumps as will not pass between the bars of the internal cage. The covering (E) for the cages is made of wood, and in two parts, the upper part being arranged so that it can be readily removed by lifting it off from the lower part when the cages require to be got at. This cover (E) has an opening opposite the internal cage, through which the materials is passed which is to be operated upon, and openings are also left in the casing (E) at E1 for the removal of the material disintegrated. This machine is most conveniently worked when it is placed on a floor, so that the material operated upon will drop down spouts into receptacles placed below the floor.

Valuation of Superphosphate.—The quality of superphosphate found in commerce varies extremely, according to price, materials used, care in manufacture, and, unfortunately too often, according to the elasticity of the conscience of the vendor. Hence, analysis, together with examination of its external appearance and mechanical condition constitute the only safe guides in its purchase, unless it be procured from makers of established reputation. We have seen samples turned out from extensive and handsomely built establishments, which are to be seen depicted in glowing colours in railway stations and other public resorts, nevertheless, of the most inferior description, and worth but a fraction of the price charged to the consumer. Of 171 samples, analyzed by Way,

11	samples	contained	5 per cent.	soluble	phosphate,
49	„	„	5 to 10	„	„
60	„	„	10 to 15	„	„
40	„	„	15 to 20	„	„
11	„	„	over 20	„	„

The following are given by various authors as analyses of samples of "Superphosphates," the first two being very inferior, the last two of excellent quality :—

	1	2	3	4
Water	14·40	13·79	10·80	0·91
Organic matter	8·91	15·00	4·21	...
Soluble phosphate . . .	3·60	2·84	20·28	25·70
Bone-earth, rendered soluble by acids	(5·61)	(4·43)	(31·63)	(40·11)
Insoluble phosphate . .	6·83	25·54	4·11	6·68
Sulphate of lime . . .	44·23	26·33	46·63	55·43
Alkaline salts, mostly common salt	2·52	4·36	10.78	7·96
Insoluble siliceous residue	19·51	12·14	3·19	2·32
	100·00	100·00	100·00	100·00
Percentage of nitrogen equal to	1·44	2·45	·34	...
Ammonia	1·75	2·91	·41	...

The following data per ton in pounds sterling have been adopted by different chemists for estimating the value of superphosphate of lime.

	Anderson.	Nisbet.	Way.	Hodges.	North British Agriculturist.	Voelcker.
Nitrogen		74				
Ammonia . . .	60 0 0	60	50 0 0	50 0 0	56	60 0 0
Insoluble phosphates . . .	7 0 0	8	7 0 0	7 0 0	7	10 0 0
Soluble phosphates	30 0 0	24	32 13 0	25 0 0	23	30 0 0
Biphosphate of lime	46 16 0					
Alkaline salts . .	1 0 0	1	1 0 0	1 0 0	nil	1 5 0
Organic matter .	0 10 0	1	1 0 0	0 10 0	nil	1 0 0
Sulphate of lime .	1 0 0	1	nil	nil	nil	1 5 0

The quantity of each ingredient in a given analysis is multiplied by its price per ton in any of the above lists, and the sum total

gives the value of 100 tons, from which the value of a ton of the superphosphate is easily ascertained.

The difference in the data adopted by chemists can only be explained by the fact that, being neither merchants nor manufacturers, they have to a certain extent founded their data on theoretical assumptions. Some makers use common salt, others employ sulphate of soda, and yet some of the chemists lump them all under alkaline salts at £1 per ton, while one party considers them of no value at all. Again, the cheapest drier the manufacturer can use is sawdust, which cannot be purchased under £1 per ton, and yet it is generally stated as worth only 10*s*. Lastly, no allowance is made by any party for the expences of mixing, bags, &c., &c. We believe that manufacturers have many just grounds of complaint as to the arbitrary way in which their produce is now valued, and it would be to their advantage to combine together to introduce a more correct system into their trade.

The importance of the trade in phosphatic manures, is shown by the very large quantities of raw materials raised in this country or imported from abroad. The following table gives an estimate of the quantities of these materials annually consumed:—

Cambridge coprolites	60,000 tons.
Suffolk coprolites	10,000 „
Mineral phosphates, apatite, &c. . . .	5,000 „
Bones, bone ashes, animal charcoal . .	80,000 „
Guano	200,000 „

And the money values of these materials when manufactured cannot be less than—

Guano	£2,500,000
Superphosphate of lime, 250,000 tons at £7	1,750,000
Bones, as bone-dust, &c., 50,000 tons at £6	300,000
	£4,550,000

The following method of estimating phosphoric acid in coprolites, bone-ash, and manures, is both expeditious and accurate:—

1. The substance is dissolved in as small a quantity as possible of hydrochloric acid; excess of ammonia is then added, the precipitate redissolved in acetic acid, and some acetate of ammonia added to the solution.

A solution of acetate of uranium, made by dissolving ammonia-carbonate of uranium in acetic acid, is finally added and the liquid boiled.

A greenish yellow slimy precipitate falls, which contains the whole of the phosphoric acid. It requires, from its character, the following treatment:—Set aside the hot solution on a sand heat, and allow it to settle completely; decant, add more water, boil, and so forth, until the precipitate has assumed a crystalline appearance, when it may be cast on the filter, without fear of choking the pores of the paper, and well washed.

The precipitate is dried and ignited, when the ammonia is expelled and lemon-coloured phosphate of sesquioxide of uranium remains, of formula $2U^2O^3 . PO^5$. This precipitate is allowed to cool, moistened with nitric acid, re-ignited, and weighed.

The analysis may also be performed in the following manner:—

2. The hydrochloric acid solution is decomposed by acetate of ammonia, and from the filtrate containing free acetic acid, the lime is eliminated by oxalate of ammonia. The phosphoric acid is determined in the filtrate by sulphate of magnesia, ammonia, and chloride of ammonium.

3. Müller's method is applicable to all substances not containing alumina, and may be used either for the determination of soluble phosphates in a *watery* solution, or of insoluble phosphate, or of a mixture of the two, a solution being first obtained, in the latter case, containing only free acetic acid, by the method described in the first method of analysis above given. A known quantity of a graduated solution of perchloride of iron is then added, next excess of ammonia, then excess of acetic acid, and the liquid boiled. The precipitate contains the whole of the phosphoric acid, and a large excess of peroxide of iron. The amount of iron present, if any, in the substance is then determined accurately, and this quantity, together with the amount due to the perchloride used, being deducted from the total weight of the precipitate, the balance represents the phosphoric acid.

The number of patents taken out for improvements in the manufacture of artificial fertilizers is so great, that we cannot consistently with the size of the volume do more than refer the reader to the Blue Books, and to the volume of abstracts of Manure Patents published by the Commissioners of Patents. A list of them will be given in the Appendix to this volume.

ARTIFICIAL MINERAL WATERS

Had their origin in the efforts of medical men to imitate the healing effects of some natural waters distinguished for their beneficial action on the human system.

These artificial mineral waters are partly imitations of natural ones prepared according to the results of the most accurate chemical analyses by means of suitable apparatus, and partly certain saline solutions prepared according to an empirical formula for medicinal purposes, such as Soda water, Carrara water, &c., &c.

The first attempt of this description was made by Thurniesser in 1560, which was followed by those of Hoffmann in 1685, and Geoffroy in 1724, but without much success; it was only, however, on the suggestion of Venel in 1750 to employ a solution of carbonate of soda in muriatic acid in a close vessel, that this art can be fairly said to have taken a step in the right direction.

In 1772 Priestley first suggested the employment of water impregnated with carbonic acid, and Bergmann, in 1774, published an account of the artificial preparation of the Selters and Pyrmont waters, in which he proved that the refreshing taste of these mineral waters was due to the carbonic acid which they held in solution. Booth improved Priestley's process in 1775 by the construction of a better apparatus, and in 1787 Meyer had already commenced the manufacture of Selters waters in Stettin on a large scale. Paul erected a similar manufactory in 1799 in Paris, and introduced the use of a pump. Suave commenced his first establishment in 1815 in Dresden; since then he has introduced numerous improvements, and is the author of several important observations on the constitution of mineral waters.

Simple Gaseous Water or artificial Seltzer Water.

Like everything new, artificial mineral waters have had their period of fashion, but at present the use of the greater part of them is very small. There is, indeed, only one of them of which the consumption can be said to be large and increasing. This is simple acidulated water, improperly called *Seltzer Water*. It is, therefore, to this that we shall particularly direct our attention. The preparation of this water is at present pushed to its utmost limits. There is not a manufacturer of mineral water who has not introduced some happy modifications into the earlier processes,

and we shall be fortunate if, in giving a history of the methods actually in practice, we can describe the numerous improvements introduced into this manufacture.

There are two methods of conducting this preparation. The first consists in placing in the water a mixture of substances which, by acting on each other, produce carbonic acid, which is dissolved in the water; the second has for its object to dissolve in pure water carbonic acid equally pure and produced in a separate apparatus.

FIRST METHOD.

This method is of ancient date. Monnet made use of it in 1775 by treating tartar with sulphuric acid. Hulme followed a nearly similar process: he made a mixture of two solutions, the one containing a fixed alkali (alkaline carbonate), the other sulphuric acid. This principle is the same as that followed at the present time for the preparation of effervescing powders, which are nothing more than citric or tartaric acid and bi-carbonate of soda.

A great inconvenience in these waters is the introduction of alkaline salts into the mineral water itself, salts which often give it purgative properties. It is unnecessary to enter into further details.

SECOND METHOD.

A first condition in this class of preparation consists in the purity of the water. It is advisable to use water which has been rendered clear through beds of sand and charcoal. Further, the use of cocks and pipes of copper or lead should be avoided, as they may impart poisonous qualities to the water.

The carbonic acid is prepared in various ways, sometimes by the calcination of earthy carbonates, sometimes, and this is most frequently the case, by the action of an acid upon a carbonate. Carbonate of lime, from its moderate price, deserves the preference; it is abundant almost everywhere, and, according to the locality, it is used in the form of washed chalk, lime, or marble. The last-mentioned substance presents a great advantage pointed out long ago by Franklin, viz., that it effervesces less violently with acids than the less compact forms of carbonate of lime. On the other hand it is less easily pulverised; and therefore the substance known under the name of Spanish white, and sold in the form of round cakes, is frequently used. This product is nothing more than pulverised chalk, washed and dried, and

moulded into this particular form; the washing destroys the argillaceous smell often present in the chalks. According to the apparatus employed, preference is given to hydrochloric or sulphuric acid; but as the gas during its disengagement frequently carries over portions of acid or extraneous matter, which renders the produce impure, it is indispensable to wash the gas before dissolving it.

To saturate the water with gas two methods are adopted. The gas passes into the water and saturates it by its own pressure, which is the method followed in the different systems recommended by MM. Vernant, Barruel, Savaresse, Ozouf, and Gaffard. Sometimes it is drawn by a force-pump into a gasometer, where it remains at the ordinary pressure, and is afterwards forced into another reservoir, which is closed and filled up with water; this is the process most generally adopted.

It would require too much space to describe all the kinds of apparatus which, at various times, have been proposed for the manufacture of acidulated waters; we shall merely state that many authors, Parker, Nooth, De Vignes, Woolf, Welter, Brugnatelli, Gilbert, Fierbingers, and others, have recommended several; we shall confine ourselves here to noticing such as are entitled to a preference, and endeavour to describe the successive modifications which have rendered their use so general. We shall also notice the methods at present proposed to enable the apparatus to sustain a continued action instead of an intermitting one, thereby producing in a given period a much smaller quantity of gaseous water with an unavoidable loss of a portion of carbonic acid.

Apparatus of Savaresse.

The apparatus of M. Savaresse is recommended by many important qualities; it is not of large dimensions, and can be easily worked in a small space; further, it is so constructed as to render an explosion impossible; the quantity of gas is known beforehand: for, in this case, the apparatus cannot be placed in operation until the excess is disposed of; lastly, the apparatus offers a resistance ten times greater than that of the gas produced by it.

The first apparatus constructed by Savaresse, while it produced artificial gaseous waters in considerable quantities, had one

inconvenience, that the action was not continuous. To remedy this defect the inventor has constructed an apparatus represented by Fig. 103, which possesses the advantage of a continuous action. Its construction is similar to that of the simpler apparatus with this difference: the receiver A, destined to furnish the carbonic acid, is increased in size so as to be able to contain 4 kilogrammes of acid and an equal quantity of carbonate of lime (blanc d'Espagne). On the table which supports the several pieces of the apparatus, a second cylinder N′ has been added independent of the first N.

The two cylinders receive the gas by means of the two columns J J′, connected with each other under the table by a tin tube. These cylinders are worked alternately, and no time need be lost except such as is required to recharge the recipient A.

When the water in the cylinder is sufficiently saturated, the latter (we speak of that on the right hand) is placed in the position it occupies in the figure; the cock P is then opened in order that the water may pass to the bottling apparatus. When this cylinder is empty, it is returned and placed in the position represented by N, which admits of its being easily filled. This operation is effected in about ten minutes by means of the pump D placed on the table of the apparatus. To the second cylinder N′ is attached a manometer O.

To the apparatus is attached a bottling apparatus, either that of Stevenaux, or of Vieil-Cazal. Several of these apparatus may be attached at the same time by means of the tubes *a*, *a′*, *a″*; in the latter case, the conducting tube, instead of using the cock P or P′, is fitted to a piece which is attached to the table between the two cylinders, which may be turned so as to communicate alternately with each of them. According to the cylinder which is in operation, the cocks R and R′ may be opened or shut at will. These two cocks serve also to establish or cut off the communication with the tube *b*, which comes from the pump and conveys the water intended to be saturated.

Apparatus of Ozouf.

This apparatus is constructed in the following manner: In the interior of a metallic cylinder C the carbonic acid gas is produced by the reaction of sulphuric acid on marble or chalk;

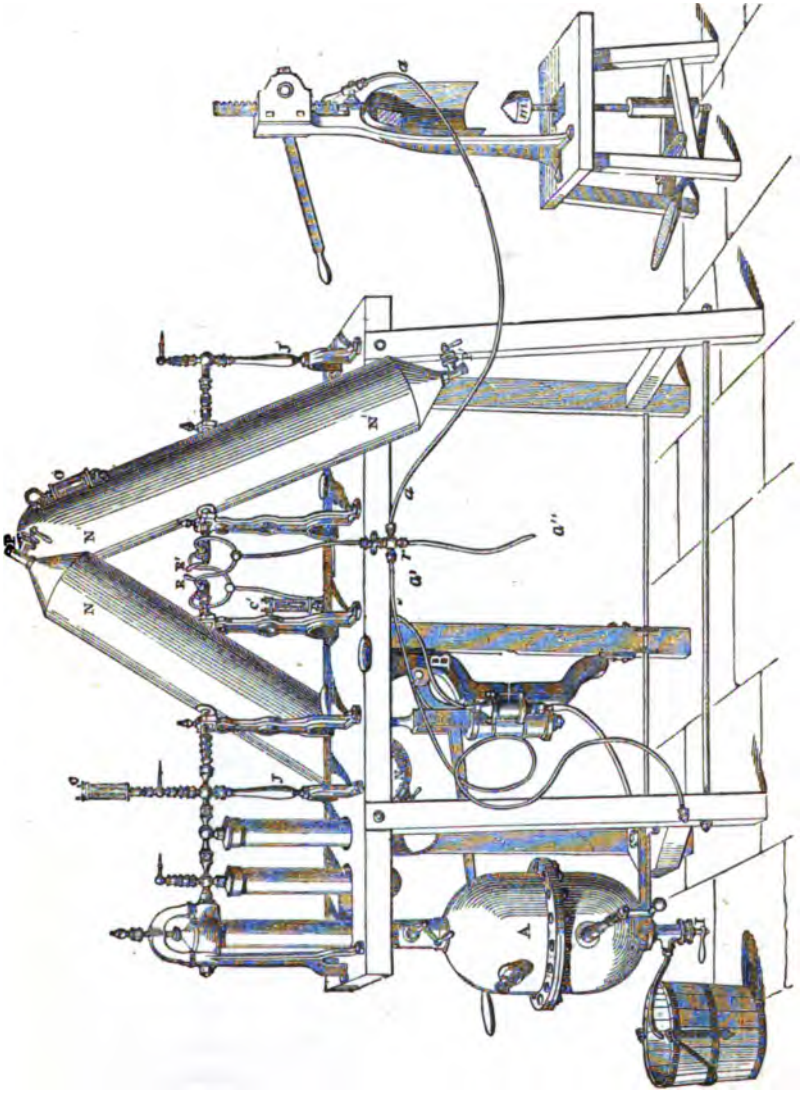


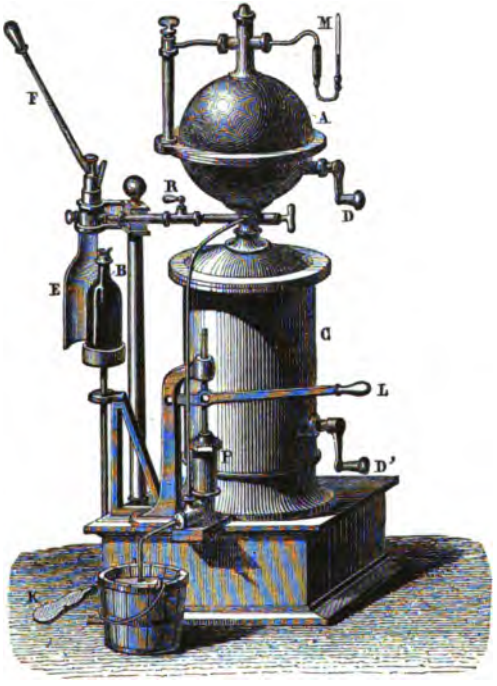
FIG. 103.

the acid is contained in a leaden vessel placed in the upper portion of the cylinder, and is poured upon the carbonate of lime in the lower part by means of a valve. The reaction is facilitated by means of a handle D', which sets in motion an agitator furnished with paddles; the disengaged gas passes through a washing apparatus contained in the interior, and thus arrives, after passing the pedestal uniting the two parts of the apparatus, at the upper part. This consists of a globe of copper, formed by two hemispheres well tinned in the inside, each furnished with a flange, so as to form an hermetically closed joint, firmly held together by two rings of iron and screw-bolts. This globe is furnished on one side with a gauge M, showing the pressure; on the other, with a hollow glass tube communicating with the globe at the lower part, and marking, by the height of the water it contains, the level of the liquid in the globe. By means of the handle D, an agitator is set in motion, which mixes the gas with the water and facilitates its solution. On the pedestal is fixed the pipe furnished with the cock R, through which the gaseous water passes. To fill a bottle it is placed on a block of wood, which can be raised or lowered at will by means of the pedal K. This bottle B is covered with a metallic shield E, which, in case of explosion, protects the operator from the pieces of glass. The mouth of the bottle is placed in communication with the tube by which the gaseous water passes on opening the cock R. When the bottle is full, it is corked rapidly by the corking machine set in motion by the lever F. In well-mounted apparatus, the globe A is filled with water, by means of the pump P, so that should any gas remain from the preceding operation, it is not lost, but dissolves immediately in the water. When this pump is not present, a loss is to be feared; it is necessary to recharge the globe by the opening in its upper part, which, as it communicates with the air, allows the excess of gas to escape. One of the great advantages of this apparatus, is the small space it occupies; a space 2 metres high by 1 wide (or 6 feet by 3 feet) being quite sufficient.

Besides this apparatus, M. Ozouf, who has minutely studied everything relating to this class of industry, has perfected his method by several improvements. The first consists in what he calls a *continuous* apparatus; it completely effects the purpose —*that of obtaining the largest quantity of produce in the smallest volume and in the shortest time possible.* This appa-

ratus is composed of one or more pumps, which constantly refill the reservoir of water as the gaseous water is drawn from it. The pumps are set in motion by means of a steam engine of one or two horse power, which at the same time removes an agitator for the purpose of aiding the solution of the gas in the water. The carbonic acid is provided by a gasometer separate from the rest of the apparatus.

FIG. 104.



Under the name of a *continuous intermittent* M. Ozouf has constructed another apparatus realising in itself the known advantages of the continuous apparatus properly so called; that is to say, the non-solution of continuity in the manufacture, and those of the intermitting apparatus, viz., the complete saturation of the water with carbonic acid.

This apparatus is composed of:

1st. Two cylinders for producing carbonic acid;

2nd. Two washing cylinders for purifying the gas;

3rd. A column surmounted by a spherical receiver in copper, and armed with a drawing and force pump and agitator;

4th. Lastly, with all the other accessories for the fabrication, such as manometer, water level, safety valve, &c.

The pump in this apparatus also works simultaneously with the agitator and the producing cylinders, furnishing the gas alternately, one being at work while the other is charged; so that there is no stoppage in the manufacture.

We must also notice two other improvements by the same inventor: the first consists in passing the water and gas through a refrigerator of cold water before their arrival at the sphere of copper; this is especially necessary when the manufacture is carried on in summer, as the power possessed by water of absorbing carbonic acid diminishes as the temperature rises. The second consists in the use made of the carbonic acid which remains in the syphons after the water is drawn from them. By means of an ingeniously contrived cock, the bottles, after they have been filled with gaseous water, are placed in communication with a cylinder, which receives the excess of carbonic acid replaced by the liquid. The gas then passes to the gasometer. With the apparatus of M. Ozouf, ordinary bottles may be filled, or the patent bottles invented by himself.

Apparatus of Gaffard.

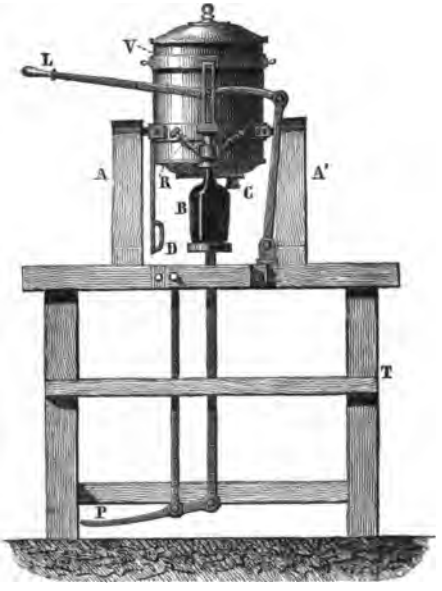
We have already mentioned that carbonate of lime is the salt most generally employed in the preparation of seltzer water, but it is not the only one; carbonate of soda has also been used in this manufacture, and principally by M. Gaffard, a druggist of Aurillac, who has also constructed an ingenious apparatus, of which we shall say a few words. This apparatus, represented in Fig. 105, is founded on the principle applied by Thilorier in his researches on the liquifaction and solidification of carbonic acid, that is to say, after he had operated by the action of sulphuric acid on carbonate of soda.

The essential parts are a receiving cylinder V, resting on two pillars of iron or wood A, A' by means of two gudgeons, on which it can be made to turn by means of the lever D. The pillars are firmly fixed to the table T, T'. At C there is an opening, through which is introduced the liquid required to be saturated with gas.

The first operation consists in turning the receiver, so that the

opening C shall remain uppermost; the cover is then taken off, and the receiver is seen to be formed of two concentric cavities; the exterior one is intended to contain the water to be saturated; the inner one called the *conductor* is made of copper. A leaden cylinder, in which the carbonic acid is produced when the apparatus is returned to its proper position, is called the *generator*, and fits easily into the conductor; the carbonic acid gas passes between the two cylinders in order to enter the water to be saturated. In the generating cylinder, a vessel of lead is placed, occupying about half the height. This vessel

FIG. 105.



contains the sulphuric acid, and is furnished at its upper part with a valve, which, when the cylinder is properly arranged, occupies the lower part of the vessel, and allows the acid to run out. Below this vessel is placed a second, which serves as a cover, and is filled with carbonate of soda. This is pierced here and there with holes to allow the gas to escape. An accessory to the apparatus, which must not be neglected, consists of a syphoid bottle of tin, the use of which will soon be seen.

To set the apparatus to work, the exterior portion of the

receiver is filled with water; the leaden vessels, charged as above described, are placed in the generator; and the syphoid bottle is filled with water by placing the extremity of the tube B in the tube C. The apparatus is now to be closed by means of proper screws; then rapidly turned and replaced in the position indicated in Fig. 105, and the syphoid bottle full of water, adjusted to the bottling tube by means of the pedal P. This tube is in communication with two cocks: one, R, conveys the gaseous water to the bottle, whilst the other gives exit to the air contained in the latter, and conveys it to the upper part of the receiver. The air contained in the apparatus is driven off by the carbonic acid, which is disengaged, and which also drives before it the water contained in the syphoid bottle. As soon as the whole of the liquid has passed through the tubo, and the gas in its turn commences to escape, the cock is quickly closed, the bottle removed, the apparatus gently oscillated for some minutes, and the bottling commenced.

In his last apparatus, M. Gaffard has added a sort of supporting bridge of metal, which can be raised or lowered at pleasure. When it is raised, the apparatus remains fixed, and the lever L can be manipulated with ease.

The bottling is effected by covering the bottle with a kind of metallic protecting shield. By opening the two cocks, one of which conveys the gaseous water, and the other allows of the escape of the air, the bottle is filled; then, by the aid of the lever, the cork is forced in, having been previously placed in the press covering the throat of the bottle. The cork must then be wired by any of the processes in use.

Geneva Apparatus.

The second system—namely, that in which the gaseous carbonic acid is procured from a gasometer, and forced into the water which dissolves it, will now be explained.

The first apparatus of this kind was established at Geneva, and afterwards at Paris by Tryaire; it has since been known by the name of the *Geneva Apparatus*. It consists of a glass or wooden vessel A, Fig. 106 (Fig. 1), lined with lead, into which the sulphuric acid is run through the opening *a'*. The supply of acid to the lower vessel B is regulated by the cock *b'* and the pipe *b*. The same pressure is maintained in both vessels by the open pipes *a a*.

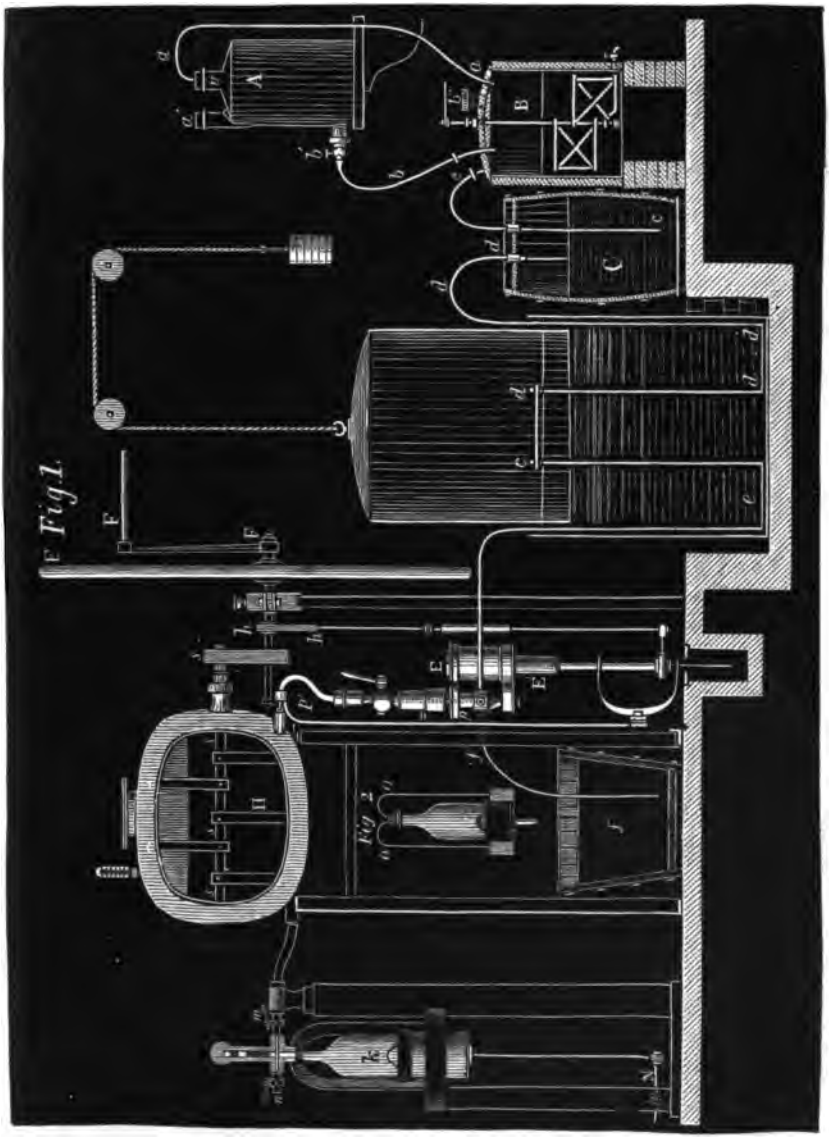


FIG. 106.

The vessel B is made of cast-iron, lined with lead or copper, and is charged with the chalk or carbonate of lime mixed with water through the opening *b'*. An agitator is fixed in the centre and moved from the outside by a handle, which prevents the chalk from settling to the bottom, and facilitates the action of the sulphuric acid. The carbonic acid which is evolved passes off through the tube *c c*, into a barrel lined with tinned copper, and partially filled with water. Any sulphuric acid or other impurities carried over mechanically are retained, and the purified carbonic acid passes into the gasometer E by the tubes *d d d*.

A pump E' withdraws the gas from the gasometer, and is worked by a handle F and excentric *h*, with a fly wheel F to give regularity to the motion. The carbonic acid passes through a tube *e e* towards the cock *p*, which admits it to the pump E. The pump then forces the gas through the tube and cock *p p'* into the condenser H. The same pump draws a supply of water by a pipe *f'* from the trough *f*, and also forces it at the same time to the condenser H. The cock *f* thus regulates at pleasure the relation between the supplies of carbonic acid and water.

The solution of the gas is assisted by the agitators *s s s*, which are made to revolve with each stroke of the pump by means of the pinion *s'*. The degree of saturation or amount of pressure is shown by an indicator, with a column of mercury, which marks the pressure in atmospheres. The liquid is generally drawn off, charged with gas under a pressure of 6 or 7 atmospheres. If the pressure diminishes, the cock *p* is turned so as to increase the supply of gas or water, should the pressure increase.

The bottles are enclosed in a casing to protect the workman against any accidental fracture. The bottle K is placed under a sheet of caoutchouc, in the centre of which there is a small funnel resting on the edges of the neck of the bottle; and a moistened and soft cork is placed each time in a cavity *l* above the channel through which the aerated water flows. The cock *m* is opened for the passage of the water into the bottle, while the air escapes through the cock *n*, which is opened for a moment for this purpose.

As soon as the bottle is filled to the neck, the cock *m* is closed, and by means of a lever the cork *l'* is forced through the funnel into the neck of the bottle, where it swells and completely closes it. The bottle is withdrawn by depressing the lever N, and placed between two bars of iron *o o'* (Fig. 2), which retain the cork

O
7

in its place while it is secured by wire or strong twine to the neck of the bottle.

M. Savaresse first suggested the use of stone-ware bottles furnished with a syphon and cock, which avoids the necessity of corking.

The apparatus now most generally used in England is that invented by Messrs. J. Tylor and Sons, Warwick Lane, Newgate Street, London, and represented in Figure 107.

These machines are made in sizes to produce 380, 200, 170, 100, and 24 dozen per diem.

The arrangement of the machine consists of a very carefully constructed gun metal pump C with valves of the same material, having their supply regulated by the taps at M, L, that at M being for water and L for gas.

A very strong condenser D, thickly coated with pure tin with an agitator inside driven at great speed by spur wheels, is fixed on the top of the pillar with the necessary inlet pipe from pump and discharge pipe to the bottling nose N. A provision is made for connecting the bottling machine, Fig. 109, with this condenser D. A solution pan O is for water-supply to the pump. A wooden gasometer tub 3, with copper rising and falling bell A, to contain gas. A leaden generator 2, for containing the whiting and water, with a swinging bottle 1, for containing the sulphuric acid.

The machine being screwed down, and the gasometer 3 and solution pan O being fixed on frames as represented in the cut, the process of manufacture is as follows:

Mix a quantity of soda and water in the proportion of one ounce of bi-carbonate or sesqui-carbonate of soda to four gallons of water. If the water is milky upon the addition of the soda, it must stand till clear, and should be drawn off a few inches above the bottom of the vessel in which it is mixed. Fill the gasometer tub 3 with water as high as the water line W. This is important, as the mouth of the pipe 4 must always be covered with water. It is only necessary to keep it to this level, the water rarely requiring to be changed. Mix fourteen pounds of pounded whiting with enough water to fill the generator 2 two-thirds full. When mixed, it should be of the consistency of cream. Pour it in through the aperture covered by the cap P. Make a solution of sulphuric, muriatic, or nitric acid, about half acid and half water, and fill the acid bottle 1 through the cap.

The gas made from either of the three acids mentioned will be equally good: but sulphuric acid is generally the cheapest.

The generator tub 3 being supplied with water, and the generator 2 with whiting and water, and the acid bottle 1 with acid solution, proceed to generate gas by swinging the acid bottle 1 gently round, causing a small quantity of acid to be discharged into generator 2, invariably turning the handle of the agitator so as to mix it with the whiting and water.

The gas generated passes through the pipe 8, up the pipe 4, and is cleansed from its impurities by passing through the water with which the mouth of the pipe is covered. The copper bell A will fill with gas. It will be necessary to blow off the first charge of gas out of the gasometer bell A through the cock 6, to get rid of the atmospheric air; the pungent smell will indicate when the gas is pure. Now turn the handle J of the machine, having regulated the supply of gas and water to the pump by means of the cocks M L. The gas will be drawn through the pipe G out of the gasometer at 5, and the water out of the solution pan O, and thoroughly impregnated with gas in the condenser D.

One man at the handle will turn it round easily at the rate of 60 revolutions or more per minute, and an experienced bottler will draw off the soda water at the rate of six dozen per hour or more. With the bottling machine (Fig. 109, page 249), any active man without experience will be able to bottle off nearly as fast as an experienced bottler by hand.

Getting rid of the atmospheric air and agitating under great pressure are the main points to be attended to in making a mineral water highly charged and of fine quality.

No solution containing saccharine matter must be passed through the machine.

There are many points of detail in manufacturing Soda Water, which are fully explained in a pamphlet given on application by Messrs. Tylor.

A machine of somewhat similar construction to that of Messrs. Tylor has been used for some years in France, where it is known by the name of *Bramah's apparatus;* it does not appear to be used in this country.

Receipts for making Aerated Waters.

The following receipts for the preparation of various aerated waters have been kindly communicated by Messrs. Tylor.

Soda Water.—The quantity of carbonate of soda usually employed is 1 oz. to 1 gallon of spring water: ¼ oz. more or less makes it highly carbonated or acidulated to suit the palate. After mixing and allowing to stand one hour, run into solution pan through a lawn strainer.

Lemonade Syrup.—1 gallon hot water; 12 lbs. loaf sugar; ½ lb. tartaric acid; ½ oz. essence of lemon. Strain through flannel while warm, put in ¼ gill to each bottle, and bottle aerated water upon it from machine. No soda is to be used in making this aerated water.

Seltzer Water.—10 gallons water; 2 oz. lime; 2 oz. carbonate of soda; 4 oz. common salt. To stand and settle twelve hours before being used. To be passed through the machine in the same manner as soda water.

Potassa Water.—10 gallons water; 5 oz. carbonate of potash. Settle twelve hours. Pass through machine.

Magnesia Water.—10 gallons water; 5 oz. magnesia. Settle twelve hours. Pass through machine.

Ginger Beer.—Boil 10 oz. old ginger "bruised" in 5 quarts water for twenty minutes, skim it, add ½ oz. dried red capsicum and 6 lbs. loaf sugar. Boil for twenty minutes more, keeping it carefully skimmed. Add ½ oz. essence of lemon on a lump of sugar. Stir up and pour through a flannel bag while lukewarm, and put in 1 oz. more or less to each bottle, according to taste, and bottle aerated water upon it from machine. No soda is to be used in making this aerated water. Nothing containing sugar or saccharine matter is to be passed through the machine.

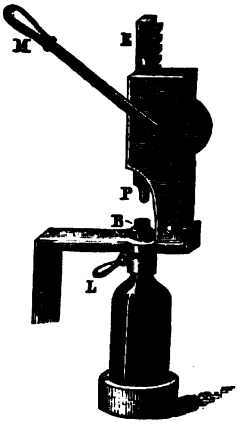
Bottling and corking of Gaseous Waters.

When a bottle is full the corking is proceeded with. The corking of the bottles is not without interest, as it is of great importance that the liquid should remain fully charged with carbonic acid.

Many methods of corking have been adopted, all having for their object to force in the cork as much compressed as possible, so that when left to itself it may quickly resume its original form, and adhere strongly to the internal surface of the neck.

The first method, invented by M. Stevenaux, is shown in the apparatus Fig. 108. It is a species of rack E, similar to that of a lifting jack, terminated by the point P, which when set in motion by the lever M presses upon the cork B: the latter, having been previously placed in a species of press of smaller diameter, is equal to that of the bottle, which has been fixed at the lower part by means of a vice L.

FIG. 108.



The machine itself is fixed to an immoveable table, and the bottle is brought to the proper position for corking, by placing it on a cone of wood, which is moved by a pedal.

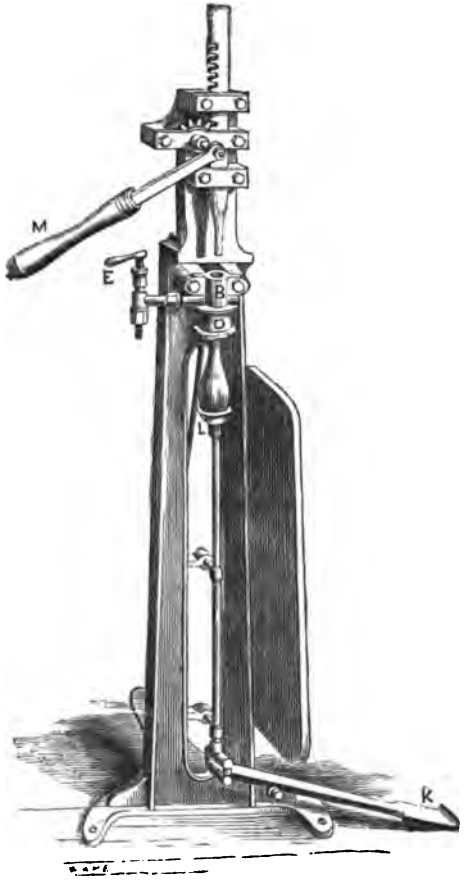
The system of corking of M. Viel-Cazal adapted to the apparatus of Savaresse and Ozouf is formed by a long lever, which, on being pressed on the cork, forces it into the neck of the bottle.

The corking should not be proceeded with so long as the water remains turbid. This phenomenon, which has been explained by M. Boissenot, is caused by the presence of small gaseous bubbles in the liquid; it is requisite to wait a moment, keeping the mouth of the bottle pressed against the india rubber; when the transparence is re-established, the bottle may be corked.

Fig. 109 represents a bottling machine constructed by Messrs. Tylor. This machine being secured to the floor, the bottler takes his place on the outside of the mahogany guard-board, the corks being previously well soaked in water. The bottle is then placed on the cup L, and by putting the foot on the treddle K, the mouth of the bottle is raised in the chamber D against the leather collar, which prevents any escape. The wetted cork is then placed in the opening at the top of B, and the handle M is raised, so as to make the plunger of gun-metal press lightly on the cork. The operator keeps hold of the handle with his right hand while he opens the cock E with his left, and when the bottle is nearly filled, the cock E is turned off, and the handle M brought sharply down, so as to force the cork into the bottle with a blow like that of a mallet. The treddle must at the same itme be firmly pressed with the foot, otherwise the downward

pressure will force the bottle away instead of driving the cork in. The bottle is then passed quickly to the person who secures it with twine or wire.

FIG. 109.



Wiring the Bottles.

The pressure of the gas contained in the water is always tending to drive the cork out of the bottle, and, notwithstanding the swelling of the corks and their adherence to the inner surface of the bottle, it not unfrequently happens that they are driven out with violence; in order to avoid this inconvenience, it is customary to wire the bottles, either with fine strong cord

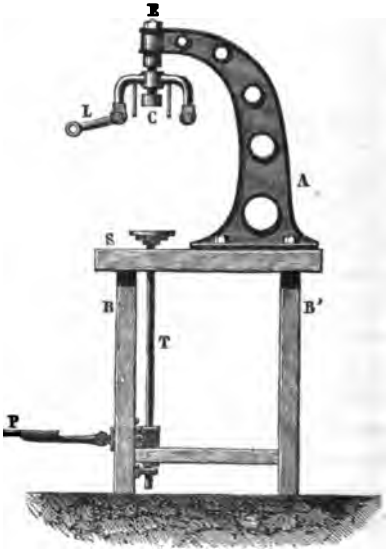
or, better, with iron wire. The apparatus shown Fig. 110 is well contrived for retaining the cork in the neck of the bottle whilst the wire is being put on. It is the invention of M. Gaffard, and is composed of a cast-iron support S curved at its upper part, through which is worked a screw moved by the lever L. This screw is terminated at its lower extremity by the flat piece P, which presses on the cork B, previously forced into the neck of the bottle. The latter is enveloped by a wire C, which passes through a slit in P; it is then only necessary to fasten it strongly, so that the cork being well supported may swell out above the neck: the screw is then removed, and the operation is finished.

FIG. 110.

Pitching and Capsulage.

The bottles having been wired are next to be pitched; but at present, especially for bottles destined for exportation, it is customary to cover them with a leaf of thin metal, to which operation the name of *capsulage* is given. The capsules generally in use are of lead or tin; the choice of the metal is not a matter of indifference; in fact the lead may in process of time become converted into the carbonate of this metal, which is poisonous; it is, therefore, preferable to employ tin, which is free from any inconvenience of this sort.

FIG. 111.



The Capsulage is executed as follows: the cork is covered with a spherical metallic cap, which is pressed hermetically against the neck of the bottle by the aid of a turn of cord. This cord, which is strong and about ½ inch in diameter, is stretched and fixed firmly to the bottom by one of its extremities. The other end is fixed to a pedal which the operator presses with his foot so as to stretch the cord to the extent desired. The cord taking a turn round the neck of the bottle, and being tightly stretched, forces the sides of the metallic capsule to adhere to the glass.

Apparatus for the extemporaneous Manufacture of Gaseous Water.

All the systems hitherto described, including the methods of bottling, preserving, &c., are specially useful, when the object is to produce gaseous water in large quantities for exportation and sale. But it is often desirable to obtain small quantities of aërated water in a short time and at little cost. For this purpose several forms of apparatus have been devised. We shall first notice that of M. Briet, which is much used both in hospitals and in private establishments.

This apparatus, represented in Figures 112, 113, 114, is composed of the following parts.

The first or decanter (carafe) *a*, is a very strong glass vase, in which the water to be saturated with gas is placed. This vase is enveloped in a net work of rattan for the purpose of guarding against explosions and the projection of the glass in case the apparatus should burst; it is furnished with a socket of pure tin, which is cast upon the glass and not cemented on, as was formerly the custom. The second portion, *b*, called the *globe*, is also of very strong glass covered with a rattan netting, cemented to a porcelain stand, furnished also with a tin socket, having a cock of the same metal, and screwing into the former. Into this globe is introduced the mixture for generating carbonic acid gas. Tartaric acid and bi-carbonate of soda are generally used in the following proportions:

Tartaric acid	17 grammes.
Bi-carbonate of soda . . .	21 „

This mixture is introduced by means of a small funnel, which prevents the powders from attacking the netting. This operation being complete, the metal tube, Fig. 112, is introduced into the vase so as to close the opening completely. The globe is then screwed on, so that the apparatus, when complete, assumes the form represented in Fig. 113. It is then turned over and placed in the position represented in Fig. 114, when the following action takes place: the excess of water passes through the tube *d* (Fig. 114) and reaches the globe by the holes *c*; the bi-carbonate of soda and tartaric acid are dissolved;

FIG. 112.

FIG. 113.

FIG. 114.

and the gas disengaged by their mutual action, penetrates by the upper holes, and reaches the water in the vase after passing through a small sieve of pure silver. The gas mingles with the water and is dissolved, and, in proportion as the quantity augments, the pressure increases and larger quantities are dissolved. When it is desirable to have the water highly charged, a double quantity of the mixture may be used.

Another apparatus for the rapid production of aerated waters for

private use is that proposed by Liebig. It consists of a stoneware vessel divided into two compartments A and B, Figs. 115 and 116.

FIG. 115.

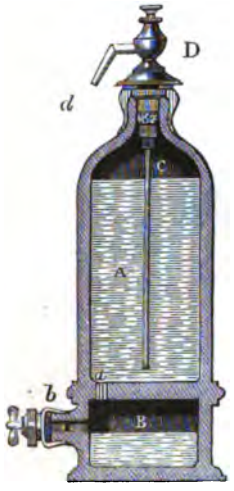
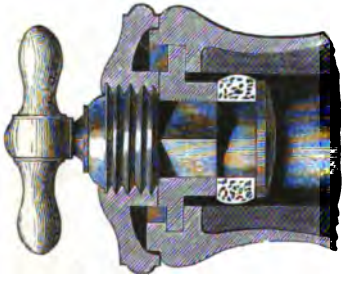


FIG. 116.

The lower compartment B is intended for the production of the carbonic acid, and is supplied with materials through the opening *b*, which is closed by a tin stopper of peculiar construction, shown in detail in Fig. 117, the ring *a* being formed of vulcanised caoutchouc.

FIG. 117.



The only communication between the two compartments is through some capillary tubes shown at *a*, which do not permit the passage of the liquid from above in consequence of their fineness, and the greater pressure exerted in B. The carbonic acid is produced by throwing bi-carbonate of soda and tartaric acid in crystals into the spaces B, which are partially filled with water. The crystals of tartaric acid slowly dissolve and generate a continuous stream of carbonic acid, which being gradually cooled is easily absorbed by the water in the upper compartment. The pressure which the gas exerts in C forces the

aerated liquid through the tube *c* as soon as the stopper D (Fig. 118) is forced down by the hand, when it may be collected at *d*.

FIG. 118.

Mr. Bakewell has patented another very simple form of apparatus in this country. It is made of stoneware and mounted on a frame. The space B (Fig. 119) is filled with liquid to be aerated by means of an aperture *f*. About three quarters of a pint of water are also poured in at *e*, which partly fills the space below the strainer *d*; then 3 oz. of coarsely pounded crystallized tartaric acid, and about ¼ lb. of carbonate of soda in powder, are introduced at the same place. The opening at *c* is now made air-tight and the vessel gently shaken, which causes the water to pass through the holes of the strainer, bringing the acid and carbonate of soda into contact so as to evolve the carbonic acid, which, passing down the tube *c i*, is forced through the small openings *i i i* into the liquid in the space B. The carbonic acid expels the air in the apparatus through *f*, which is afterwards made air-tight. The liquid is fully charged by the carbonic acid evolved

FIG. 119.

from the quantities above named, and may be drawn off by means of a cock at *g h*.

Sulphuric acid may be substituted for the water poured in at *e*, thus saving the expence of the more costly tartaric acid.

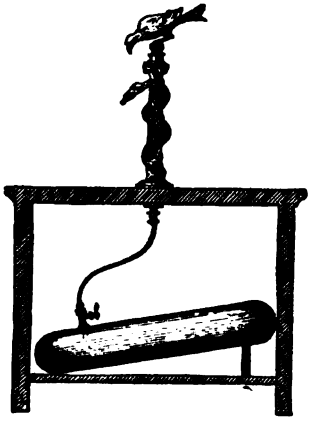
Fountains for Artificial Waters.

M. Savaresse has invented several ingenious apparatuses for this purpose. They are generally small columns of bronze, gilt or silvered, and terminated at the lower part by a small sculptured figure, which acts in the same way as the knob or lever of ordinary syphons; the interior is protected with tin, and a tube of the same metal places them in communication with a charged cylinder generally concealed under the table to which the column is fixed.

Fig. 120 represents one of these columns; the gaseous water flows out through the head of the serpent on pressing the figure,

FIG. 120.

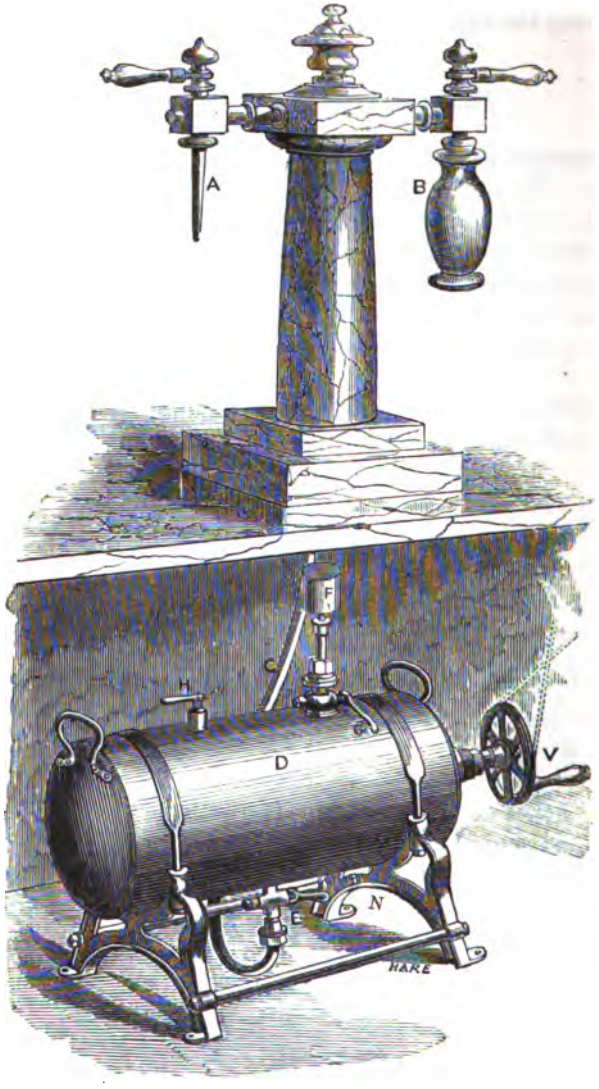
FIG 121.



which surmounts the column. Fig. 121 is a section showing the relative position of the column and the generating cylinder.

Fig. 122 represents a counter fountain, with copper supply

FIG. 122.



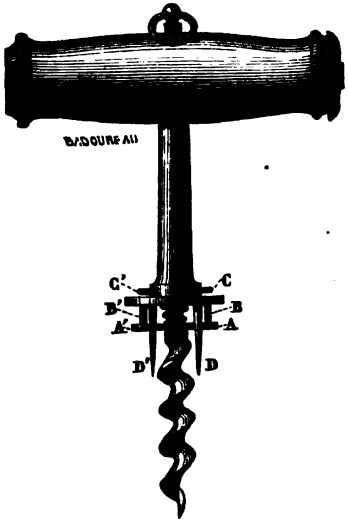
cylinder, constructed by Messrs. Tylor. The cock E is connected with a soda water machine: gas is at first pumped in for a few

minutes only, the jet cock H being left open to expel the air. When the pungent smell indicates that the air is exhausted the jet-cock is closed and the charging with gas continued till the safety-valve F lifts, care being taken that the cock G under the safety-valve is open. About half-an-hour's pumping is generally sufficient for a 6-gallon cylinder. To ascertain when the charge is complete, the jet-cock H is opened, and if it blows gas only, it is shut and the charging continued until the jet blows water. This shows that the water is at its correct height in the cylinder. If it is not sufficiently aerated to suit the palate, gas must be pumped in for a few minutes longer.

Uncorking (Mechanical Cork Screw).

We shall finish this sketch of artificial mineral waters with the description of an ingenious cork-screw invented by M. Batard for extracting corks from ordinary bottles without shaking the liquid. It may be very serviceable when it is necessary to analyse waters containing a sediment which must be collected. This corkscrew, Fig. 119, consists of: 1st, two points of steel D D′, which penetrate the cork after the lower spiral is fixed in it; 2nd, a plate A A′, furnished with two pillars, B B′, penetrating into two openings in the upper plate, and pressing against two pegs C C′, which act as a lever.

FIG. 119.



The plate A A′ is surmounted by a spring, which, in proportion as the cork-screw enters the cork, becomes flattened and allows A A′ to press against the plate above it.

When the pillars on A A′ press on C C′, it is easy to turn the cork in the neck of the bottle and extract it without the least shaking.

ARTIFICIAL MINERAL WATERS PROPERLY SO CALLED.

Although the manufacture of simple *gaseous water* is very extensive at the present time, and its consumption daily increases, in spite of the constant use of certain gaseous waters, such as those of Saint-Calmier and Soultzmatt, it is not the case with the preparation of *artificial mineral waters*, which tends to diminish continually from the following causes.

Numerous sources of natural mineral waters, as varied in their chemical composition as in their medicinal properities, are being discovered every year, especially in France. The economy with which they are at present procured, bottled, sent to a distance, and warehoused, permits of their delivery to the consumer under favorable conditions, and at a very moderate price; it is therefore natural to give them the preference; the more so, because no one can doubt that the imitation of natural waters is very difficult, and often even impossible, as they cannot be prepared exactly as nature produces them. Thus, the analysis, which serves as the base of these imitations, indicates in the natural waters particular organic matters, combined with iodine, nitrogen, and sulphur, which we cannot reproduce even approximately. Besides, the elements found are sometimes differently grouped according to the method of analysis employed for their detection; then, moreover, we are often ignorant of the manner in which the elements are united. Are they simply mixed or combined? May not the *iodides*, for example, by the side of the *sulphides* form *sulphiodides;* may not the various sulphates of *lime*, *soda*, and *magnesia* be equally combined in a particular manner, as their medicinal properties often differ from those of each of them separately.

Lastly, there are certain important constituents of mineral waters—arsenic, for example—the nature of whose combinations we do not always understand. In imitating waters, there is also a general custom of suppressing certain substances which are considered inert or useless; perhaps this is wrong, for we do not always really know how certain mineral waters act. It must, therefore, be allowed that artificial mineral waters are far from being correct imitations of the original springs; moreover, the manufacturers do not always employ identical receipts for the same class of water, but more frequently special ones, based on

analyses having little similarity to each other. Nevertheless, certain artificial mineral waters, when well prepared, have incontestable advantages in their medical application, and produce very useful results.

We must, therefore, add a short account of the processes employed for their preparation. We are of opinion that the composition of the natural waters should be imitated as closely as possible, and, to attain this end, it is necessary as nearly as may be, not to omit any of the elements found by analysis, provided they can be kept in solution. For the imitation of a particular water it is also necessary to take as a guide those analyses which most nearly approach each other. We can then make the mixtures either *directly*, especially if the salts are all soluble, or if insoluble, dissolve them by means of carbonic acid; or otherwise, as recommended by some able manufacturers, obtain by *double decomposition* certain salts which we wish the water imitated to possess. Carbonic acid is an agent capable of dissolving a large number of saline compounds, especially when the latter are found in the state of hydrates or recently precipitated; this agent is, therefore, very useful in many cases for the manufacture of artificial mineral waters. Thus *carbonates of lime* and *magnesia, carbonates of iron* and *manganese, calcareous phosphates* and *sulphates, earthy silicates*, &c., dissolve readily in carbonic acid, provided they exist in a gelatinous or hydrated condition. It is, therefore, easy to mix the whole in water charged with carbonic acid, or to procure them by double decomposition in the liquid itself.

Suppose that we wish to introduce into the water to be imitated, the *carbonates of lime, magnesia, iron*, and *manganese*: we may prepare these salts, and add them to the water as insoluble *hydrates*, in the proportions required, then employ the carbonic acid; or introduce them in the proportions indicated by theory for the imitation of the water; for instance, *chlorides of calcium and magnesium* as well as *protosulphates of iron and magnesia, and carbonate of soda: the carbonates* will be produced, and at the same time *sulphate of soda* and *chloride of sodium*.

Let us take an example from the Soubeiran's work.

The water of Saint-Nectaire contains, according to Berthier, per litre:

Saint-Nectaire Water.

	Gram.
Carbonate of soda	5·395
Carbonate of lime	0·443
Carbonate of magnesia	0·241
Sulphate of soda	0·352
Chloride of sodium	2·436
Oxide of iron	0·014

This is imitated by the following mixture :

	Gram.
Carbonate of soda	7·472
Chloride of sodium	1·591
Chloride of calcium	0·964
Chloride of magnesia	0·582
Sulphate of soda	0·352
Oxide of iron	0·014

There will be a formation of *carbonates of lime and magnesia*, as well as of *chloride of sodium ;* the water will likewise contain the excess of *carbonate of soda* and *chloride of sodium.*

With similar data, and the assistance of the practical works of pharmacy, by MM. Soubeiran, Henry père et Guibourt, Lecanu, Darvault, &c., we give the following formulæ for the production of different mineral waters most generally used.

SALINE WATERS.

Sea Water.

Sea salt	8400 grammes.
Crystallized sulphate of soda	3702 „
Crystallized chloride of calcium	765 „
Crystallized chloride of magnesium	3111 „

For a bath of 300 litres.

Water of Balaruc for drinking.

	For 1 litre.	For 1 bottle.
Bi-carbonate of soda	0·517	0·418
Chloride of sodium	5·756	3·600
Crystallized chloride of magnesium	2·412	1·517
Crystallized chloride of calcium	1·882	1·175
Sulphate of potash	0·053	0·033
Crystallized sulphate of soda	1·900	1·187
Bromide of potassium	0·040	0·025

The chlorides of calcium and magnesium are dissolved by

themselves; the saline solution is divided in the bottles, which are filled with a solution of the salts of soda and bromine, and charged with three volumes of carbonic acid.

Sedlitz Water.

	For 1 litre.	For 1 bottle.
Crystallized sulphate of soda . .	13 gram.	8 gram.
Pure water	1 litre.	625 „
Carbonic acid	4 vol.	4 vol.

Custom has fixed the use of this formula; and sedlitz water being always employed as a purgative, a more exact imitation of the *natural water* is unnecessary.

Water from Contrexéville.

	Per litre.	Per bottle.
Crystallized sulphate of lime . .	0·370 gr.	0·880 gr.
Crystallized sulphate of magnesia .	0·430 „	0·300 „
Carbonate of lime	0·806 „	0·500 „
Carbonate of magnesia	0·017 „	0·010 „
Crystallized chloride of calcium .	0·074 „	0·500 „
Crystallized chloride of magnesium	0·025 „	0·016 „
Tartrate of potash and iron . . .	0·030 „	0·020 „
Water	1000·000 „	625·000 „
Carbonic acid	5 litres.	5 vol.

Recently prepared carbonates of lime and magnesia are employed; they are mixed with care, as well as the sulphate of lime, in the solution of the other salts, then charged with carbonic acid, and bottled.

Carlsbad Water.

	For 1 litre.	For 1 bottle.
Crystallized sulphate of soda . .	5·212 gr.	3·500 gr.
Crystallized sulphate of magnesia .	0·516 „	0·340 „
Crystallized carbonate of soda . .	3·810 „	2·380 „
Chloride of sodium	0·684 „	0·450 „
Crystallized chloride of calcium .	0·673 „	0·450 „
Tartrate of potash and iron . .	0·013 „	0·008 „
Gaseous water	1100·000 „	625·000 „

The two sulphates, the carbonate of soda, and the salt of iron are dissolved; a separate solution is made of the chloride of calcium, the liquids are mixed and charged with carbonic acid.

Pullna Water.

	For 1 litre.	For 1 bottle.
Crystallized sulphate of soda . .	24·140 gr.	16·00 gr.
Crystallized sulphate of magnesia .	37·456 „	25·00 „
Crystallized carbonate of soda . .	1·959 „	0·65 „
Crystallized chloride of calcium .	2·024 „	1·20 „
Crystallized chloride of magnesia .	1·877 „	1·20 „
Chloride of sodium	2·109 „	1·40 „
Gaseous water of 5 volumes . .	1000·000 „	625·00 „

Each bottle of 625 grammes contains 41 grammes of the sulphates of soda and magnesia.

Magnesian Gaseous Water.

	The litre.	The bottle.
Magnesia alba . . .	6 gram.	4 gram.
Pure water	1 litre.	625 „
Carbonic acid . . .	6 vol.	6 vol.

It is necessary to employ the magnesia while in the humid state, as it dissolves less readily after being dried; for this purpose a boiling solution of sulphate of magnesia is precipitated by an excess of carbonate of soda; the precipitate is collected, washed with care, and drained on a cloth; a certain weight of this precipitate is then taken, dried, calcined, and again weighed. The product is pure magnesia, of which one part by weight represents 2½ parts of white magnesia in the dry state. The magnesian precipitate is then diffused through the water, charged with carbonic acid, and after twenty-four hours of contact the water is bottled.

Saturated Magnesian Water.

	For 1 litre.	For 1 bottle.
Magnesia alba	12 gram.	8 gram.
Pure water	1000 „	625 „
Carbonic acid	6 vol.	6 vol.

The operation is performed in the same manner as for gaseous magnesian water. A little carbonic acid remains in excess. The white magnesia of commerce may be used, but in this case some of the magnesia remains undissolved. If, instead of weighing the magnesia, its weight is calculated after that of the sulphate, it is necessary to employ for each litre 32 grammes of crystallized sulphate of magnesia, which is decomposed, as already described, by carbonate of soda.

A stronger magnesian water, more charged than the preceding, is made by introducing into each bottle 16 and even as much as 24 grammes of carbonate of magnesia. The dose of carbonic acid must, of course, be increased in proportion.

BI-CARBONATED ACIDULATED WATERS.

Seltzer Water.

	For 1 litre.	For 1 bottle.
Crystallized chloride of calcium .	0·50 gr.	0·33 gr.
Crystallized chloride of magnesia .	0·40 „	0·27 „
Crystallized carbonate of soda . .	0·90 „	0·60 „
Common salt	1·60 „	1·10 „
Crystallized sulphate of soda . .	0·08 „	0·05 „
Crystallized phosphate of soda .	0·10 „	0·07 „
Gaseous water at 5 vol.	1000·00 „	625·00 „

The salts of soda are dissolved in water distinct from the chlorides of calcium and magnesium; the two liquors are then mixed and charged with carbonic acid.

Vichy Water.

	For 1 litre.	For 1 bottle.
Crystallized carbonate of soda . .	14·886 gr.	10·000 gr.
Chloride of sodium	0·167 „	0·1000 „
Crystallized chloride of calcium .	0·775 „	0·500 „
Crystallized sulphate of soda . .	0·740 „	0·500 „
Crystallized sulphate of magnesia	0·246 „	0·160 „
Tartrate of potash and iron . .	0·009 „	0·006 „
Water	1000·000 „	625·000 „
Carbonic acid	5 litres.	5 vol.

The salts of soda and iron are first dissolved; the sulphate of magnesia, and then the chloride of calcium, are added; the whole is then charged with carbonic acid and finally bottled.

FERRUGINOUS WATERS.

Bussang Water.

	For 1 litre.	For 1 bottle.
Crystallized carbonate of soda . .	4·00 gr.	2·60 gr.
Crystallized chloride of calcium .	0·75 „	0·50 „
Crystallized chloride of magnesia	0·42 „	0·28 „
Crystallized sulphate of iron . .	0·04 „	0·26 „
Water deprived of air	1000·00 „	625·00 „

The solutions of the salts are mixed, and charged with carbonic acid; one centigramme of *arseniate of soda* is also introduced into this formula per litre.

Pyrmont Water.

	Per litre.	Per bottle.
Crystallized sulphate of soda . .	1·15 gr.	0·80 gr.
Crystallized sulphate of magnesia .	1·15 „	0·80 „
Crystallized chloride of magnesium	0·75 „	0·50 „
Crystallized chloride of calcium .	3·20 „	2·10 „
Crystallized carbonate of soda . .	5·60 „	3·60 „
Crystallized sulphate of iron . .	0·24 „	0·16 „
Water deprived of air	1000·00 „	625·00 „

Mix the solutions of the salts, and charge with carbonic acid.

Spa Water.

	Per litre.	Per bottle.
Crystallized carbonate of soda . .	0·62 gr.	0·21 gr.
Crystallized chloride of calcium . .	0·25 „	0·16 „
Crystallized sulphate of magnesia .	0·60 „	0·40 „
Crystallized sulphate of iron . . .	0·17 „	0·12 „
Water deprived of air	1000·00 „	625·00 „

Add the salts to the water, and charge with the carbonic acid.

SULPHUROUS WATERS.

Leamington Water.

	Per litre.	Per bottle.
Sea salt	6·290 gr.	4·00 gr.
Crystallized chloride of calcium .	2·910 „	1·80 „
Crystallized chloride of magnesium	2·290 „	1·40 „
Crystallized sulphate of soda . .	0·880 „	0·53 „
Pure water	875·000 „	547·00 „
Simple hydrosulphuretted water .	125·000 „	78·00 „

The salts are dissolved in water, which has been boiled to expel the air, and then cooled in closed vessels; the solution is filtered and introduced into bottles, which are only filled to $\frac{9}{10}$ths of their capacity; the hydrosulphuretted water is then added; and they are quickly and tightly corked.

Naples Water.

	Per litre.	Per bottle.
Crystallized carbonate of soda . .	1·600 gr.	1·00 gr.
Carbonate of magnesia	0·880 „	0·58 „
Gaseous water of 4 volumes . . .	875·000 „	547·00 „
Hydrosulphuretted water . . .	125·000 „	78·00 „

A sulphurous water with sulphide of sodium, is made by simple solution; water deprived of air, and holding in solution the remainder of the salts, with the exception of the alkaline sulphide is then added.

Barèges Water.

	Per litre.	Per bottle.
Crystallized sulphide of sodium .	0·216 gr.	0·135 gr.
Crystallized carbonate of soda . .	0·216 „	0·135 „
Chloride of soda	0·116 „	0·135 „
Water deprived of air	1000·000 „	625·000 „

Dissolve and preserve in well-corked bottles.

By a slight modification of the preceding doses, imitations of the waters of Canterets, Bagnères-de-Luchon, Saint-Sauveur, &c., may be prepared.

In spite of the tendency which natural waters have to replace the artificial ones, there is one kind of artificial water of which considerable use is still made, particularly in certain special hospitals, viz., the sulphurous baths of Barèges, which are prepared by the aid of sulphides of potassium and sodium (called livers of sulphur). They are very useful in a large number of cutaneous affections, but the composition of the alkaline sulphides is very variable and entails a corresponding variation in the composition of the baths. In fact, if the liver of sulphur is prepared in the dry way they are formed of *sulphate of potash* and *tri-sulphide of potassium;* if, on the contrary, they are prepared in the moist way, not by dissolving the preceding in water, but by dissolving 1 part of flowers of sulphur in 3 parts of caustic potash of 35 degrees, a totally different mixture formed of *hyposulphite of potash* and of *penta-sulphide of potassium* is obtained.

Sulphurous waters are also prepared by making a simple solution of sulphydric acid in water.

Anglada, who perceived that the sulphurous waters of the

Pyrenees owe all their action to the sulphide of sodium, employed this salt in the preparation of artificial waters; and in a memoir which he published on the subject he endeavours to recompose by synthesis the principal sulphurous waters so frequently made use of in therapeutics. M. Felix Boudet and M. Soubeiran have also been engaged with this subject. In a recent work, the latter has proposed a series of formulæ representing, with all the fidelity to be expected under the circumstances, the various sorts of sulphurous baths which may be imitated artificially. These formulæ, with which we shall finish this chapter, and which we derive from the memoir, as lately published by M. Soubeiran, offer to the medical man, who practises far from the thermal establishments, medicines endowed with properties identical with those of the natural waters.

Bath of Sulphide of Sodium.

Made with the mono-sulphide of sodium crystallized.

Crystallized sulphide of sodium . . .	40 gram.
Crystallized carbonate of soda . . .	40 „
Chloride of sodium	40 „

For a bath of 200 litres.

Bath of Bi-hydrosulphate of Soda.

Prepared by adding to the solution of sulphide of sodium, the quantity of acid necessary for decomposing the half.

Crystallized sulphide of sodium . . .	40 gram.
Tartaric acid	13 „
Or Bi-sulphate of potash	21 „

For a bath of 200 litres.

Dissolve the sulphur in the water of the bath, and pass gently to the bottom of the bath the tartaric acid or the bi-sulphate of potash taken in rough powder.

This bath contains bi-hydrosulphate of soda (double sulphide of sodium and hydrogen).

The physician may vary the strength at pleasure; the weight of the tartaric acid is almost exactly the third, and the weight of the bi-sulphate of potash, the half of the weight of the alkaline sulphide, which is introduced in the formula. These simple proportions, which are easily remembered, are near enough for practical purposes.

Hydrosulphuric Bath.

This is a bath of sulphuretted hydrogen. It is prepared by adding to a bath of sulphide of sodium sufficient acid to separate all the sulphur in the state of sulphuretted hydrogen.

Crystallized sulphide of sodium . . .	40 gram.
Tartaric acid	25 „
Or Bi-sulphate of potash	42 „

Operate in the manner described in the bath for the bi-hydrosulphate of soda.

The weights of the tartaric acid and the bi-sulphate of potash are double those of the preceding formula, that is to say, for the tartaric acid $\frac{1}{3}$ of the weight of the sulphur, and for the bi-sulphate equal weights.

Bath of Sulphide of Potassium.

Dry commercial sulphide of potassium, 50 gr. Dissolve for a bath of 200 litres.

This bath contains a mixture of tri-sulphide of potassium and hyposulphite of potash.

The dry sulphide of potassium may be replaced by liquid sulphide of potassium at 30 degrees, B°.

A bath with a corresponding soda base requires pure sulphide of sodium at 15 degrees in the same quantity as the liquid sulphide of potassium.

White Bath of Hydrosulphate of Potash.

It contains, besides the hydrosulphite of potash, the bi-hydrosulphate of potash and precipitated sulphur.

It is obtained by adding to the bath sufficient acid to decompose the moiety of the sulphide of potassium.

Dry commercial sulphide of potassium . .	50 gram.
Tartaric acid	16 „
Or Bi-sulphate of potash	26 „

For a bath of 200 litres.

The sulphide of potassium is dissolved in the water of the bath, and the tartaric acid or bi-sulphate of potash passed along the bottom of the bath to decompose it.

This bath contains hyposulphate of potash, bi-hydrosulphate (sulphide of sodium and hydrogen), and besides holds in suspension hydrogenated sulphur (magistral of sulphur).

The physician proportions the acid to the sulphide of potassium. It is, as in the bath of sulphide of sodium, $\frac{1}{3}$ for the tartaric acid, and the half for the bi-sulphate of potash.

Here also the dry sulphide of potassium may be replaced by three times its weight of dissolved sulphide of potassium at 30 degrees, or sulphide of soda at 25, B°.

White Hydrosulphuric Bath.

This is a solution of hydrosulphate of potash and sulphuretted hydrogen with magistral of sulphur. It is obtained by adding to the bath of sulphide of potassium sufficient acid to decompose all the alkaline sulphide.

Dry commercial sulphide of potassium . .	50 gram.
Tartaric acid	16 „
Or Bi-sulphate of potash	26 „

For a bath of 200 litres.

Operate as already directed for the bath of hydrosulphate. This bath contains hyposulphite of potash, sulphuretted hydrogen, and hydrogenated sulphur. The proportion of tartaric acid necessary for the bath, as for the simple hydrosulphuric bath, is $\frac{2}{3}$ of the weight of the sulphuret of potash, and that of the bi-sulphate of potash is equal to the weight of the sulphur, with some slight difference, which may be neglected in the formula.

It may also be prepared with dissolved sulphide of potassium or soda.

Bath of Persulphide of Hydrogen.

In this bath the solution of hyposulphite of potash holds in suspension persulphide of hydrogen with three proportions of sulphur, which decomposes slowly into sulphuretted hydrogen and magistral of sulphur.

Tartaric acid	32 gr.
Or bi-sulphate of potash	32 „
Sulphuric acid at 66°	22 „
Mix the acid in the water of the bath	200 litres.
Then add solution of sulphide of potassium at 30° .	150 gr.
Or solution of sulphide of sodium at 25°	150 „

This bath contains hydrosulphate of potash and persulphide of hydrogen, which decomposes gently into hydrogen gas and magistral of sulphur. Its principal character is in the persistence of the sulphurous odour which the sick retain after leaving the bath.

SALTPETRE AND NITRE.

THESE terms are applied to the nitrates of potash and soda, the latter being especially distinguished as *Chili-saltpetre*, from the locality in which it is found, or as *cubic nitre* from its crystalline form. At present the term *saltpetre* in technical language is for the most part applied to nitrate of potash, and *nitre* to nitrate of soda.

These salts are of great commercial importance, being consumed in large quantities and for a variety of purposes. Like all nitrates, they give off oxygen at a red heat, and serve as purveyors of oxygen to bodies capable of combining with it. Hence, combustible substances, such as sulphur or charcoal, are burnt or consumed by contact with them at a certain temperature, in the same manner as by the oxygen of the air, but generally speaking with much greater energy. It is chiefly the potash salt that is used for this purpose, because nitrate of soda is hygroscopic,* and the water which it absorbs consumes, in its conversion into vapour, a portion of the heat developed by the combustion, thereby greatly diminishing its energy. A mixture of nitrate of potash with sulphur and charcoal forms gunpowder. Baume's *quick flux* or *powder of fusion*, is a mixture of 3 parts nitre, 1 part sulphur, and 1 part sawdust, which, if set on fire in a wall-nut shell filled with it, burns with so much heat that a small silver or copper coin exposed to it is instantly melted. *Detonating powder*, a mixture of 3 parts nitre, 2 parts pearlash, and 1 part sulphur, if very dry and finely mixed, explodes when slowly heated, with a loud report, and a concussion violent enough to fracture the strongest vessels. The use of nitre as an oxidizing agent in the paste for luifer-matches has already been mentioned (p. 132), also for impregnated fusees and slow-matches. It is also much used as an oxidizing flux in the chemical laboratory and in assaying operations, oxidable substances heated with it being always brought to their highest stage of oxidation, *e.g.*, sulphur being converted into sulphuric acid, phosphorus into phosphoric acid, tin into stannic acid, antimony into antimonic acid, &c.

* According to Gentele, *pure* nitrate of soda is not at all hygroscopic, the deliquescence of the ordinary salt arising from the foreign matters, chiefly the nitrates and chlorides of calcium and magnesium with which it is contaminated. He finds, however, that gunpowder made even with pure nitrate of soda does not burn so quickly as ordinary powder. (*Dingler's Polytechnisches Journal*, cxviii. 203.)

For purposes in which the presence of moisture is unobjectionable, nitrate of soda is generally used in preference to nitrate of potash, on account of its greater cheapness, as it not only costs less, weight for weight, but is also richer in oxygen and nitrogen than nitrate of potash, on account of the atomic weight of sodium being smaller than that of potassium. 100 parts of nitrate of potash $KO.NO^5$ contain 53·4 parts anhydrous nitric acid = 13·9 N + 39·5 O; whereas 100 parts nitrate of soda contain 63·4 parts of anhydrous nitric acid = 16·5 N + 46·9 O. Hence, nitrate of soda is the salt chiefly used for the preparation of nitric acid, and as a source of nitric acid in the manufacture of sulphuric acid from sulphur, sulphur ores, &c. It is also largely used for the preparation of nitrate of potash itself, as we shall presently explain, and is acquiring continually increasing importance as a manure.

Nitrate of potash also has long been used as a fertilizer, and derives its value from the potash which it contains, as well as from the nitrogen. Nitrate of soda, on the other hand, must be considered as owing its entire value to the nitrogen, as soda is of little value to the plant; nevertheless, for the reason above stated, nitrate of soda has almost entirely surperseded the potash-salt as a manure. When of good quality, it contains about 15 per cent. of nitrogen, equivalent to 18 per cent. of ammonia, and is therefore richer in that constituent of plants than Peruvian guano. It is essentially a rapidly acting manure, and produces a marked effect within a very few days of its application; but, as nitric acid cannot be absorbed by the soil in the same manner as ammonia, it is liable to be lost unless it can be at once assimilated by the plant. For this reason, it acts best when applied as a top-dressing to grass land and to young corn. A large application has no advantage, and there can be no doubt that the best effect is produced by several very small quantities applied at intervals.

In one experiment, Mr. Pusey found 42 pounds per acre to increase the produce of barley by 7 bushels. The beneficial effects of nitrate of soda are almost entirely confined to the grasses and cereals; on clover it appears to produce no effect.

Nitrate of soda is usually sold at from £15 to £15 10*s.* per ton, and, making allowance for impurities, £16 per ton may be taken as the value of the pure salt. (Anderson's Agricultural Chemistry, pp. 229, 268.)

Nitrate of soda crystallises in rhombohedrons, which approach very nearly to the form of the cube: the crystals are anhydrous. It is very soluble in water, sparingly in alcohol. According to Max, its solubility in water at different temperatures is as follows:—

100 parts of water at	−6° C.	or	21·1° F.	dissolve	63·1	parts nitrate of soda.
„	0	„	32·0	„	80·0	„
„	+10	„	50·0	„	22·7	„
„	+16	„	60·8	„	55·0	„
„	+119	„	246·2	„	218·5	„

Hence it would appear that nitrate of soda is more soluble at 0° C. than at common temperatures; but the results require verification. Nitrate of soda, when strongly heated, gives off part of its oxygen, and is converted into nitrite of soda; afterwards the whole of the oxygen and nitrogen are expelled, and anhydrous soda remains if the air is excluded, or a mixture of soda and carbonate in the contrary case.

SOURCES AND MANUFACTURE OF NITRATE OF SODA.

This salt occurs abundantly in South America as a natural mineral. In the district of Tarapaca, Northern Chili, the dry pampa, for 40 leagues, at a height of 3,300 feet above the sea, is covered with beds of it several feet in thickness, associated with gypsum, common salt, sulphate of soda, and remains of ancient shells, the last indicating the former presence of the sea. The following description of these deposits and of the method of refining the crude nitrate of soda is extracted from Bollaert's work on Peru:

"The principal deposits of nitrate of soda yet known are on the western margin of the pampa, on the sides of some of the ravines, and in some of the hollows of the mountains of the coast, the principal refining works being at La Noria. The nitrate has not been found nearer to the coast than eighteen miles. The nitrate deposits, or *caliche*, commence about Tilidiche, extending south to Quilligaua, with interruptions of deposits of common salt, borate of soda and lime, &c. The nitrate or caliche grounds vary in breadth, the average being about 500 yards, and in places 7 to 8 feet thick, sometimes quite pure. There have been single square yards of ground which have produced nearly a ton weight of

nitrate, the layer being three yards thick. If we allow only one hundred pounds weight of nitrate for each square yard, we shall have the enormous quantity of 63,000,000 tons; so that, at its present state of consumption, there is sufficient for 1,393 years. The opinion in the country is, that the nitrate is formed from the waters which come from the Cordilleras.

A section of the nitrate ground at La Noria exhibits three distinct strata, namely, in a descending series:

I. *Costra*, or crust, composed of earthy matters, angular pieces of rock, salt, and other saline matters, about 2 feet thick.

II. *Caliche:* granular layers of nitrate of soda, containing common salt, other saline and earthy substances, and angular pieces of stone, sometimes 5 feet thick, often accompanied by much glauberite (sulphate of soda), some pickeringite (magnesian alum), mixed with earthy matters, as silica, alumina, carbonate and sulphate of lime, also iodine, bromine, chrome, and boracic acid mineral.

III. *Coba* is the general loose earthy covering to the silico-calcareous and porphyritic rocks, and here at La Noria the borate is found in nodules, from the size of a pea to two feet in diameter. In some parts of the Coba, the borate is seen in thin striæ with associated sulphate of lime. In this region the chloride of sodium and other saline matters, including borates, appear to have been formed in the Andes, and brought down by streams and by percolation. (The almost pure chloride of sodium on the mountains of the coast, is perhaps mainly derived from the salt vapours of the ocean.) There is scarcely a trace of organic matter in the soil to afford nitrogen to change the salt into nitrate: hence, it is most probable that the nitrogen is derived from the atmosphere.

The salt of the Salares or salt-beds is a mixture of various saline substances; and as there is abundance of calcareous minerals, the nitrogen of the air may give rise to the formation of nitrate of lime, which may then unite with the chloride of sodium, so as to produce nitrate of soda and chloride of calcium.

$$NaCl + CaNO^6 = NaNO^6 + CaCl.$$

The Saliteros say that one may almost see the salt of the salares transformed into nitrate. Some caliches, when quarried, are called "green," and on exposure to the air ripen, yielding the nitrate more easily. Sometimes the salt and caliche have a yellow, pink, or green colour.

Analyses of Caliche or Crude Nitre.

	Hayes.	Richardson and Browell.			
Nitrate of soda . .	64·98	43·14	36·37	27·85	6·92
Sulphate of soda . .	3·00	26·30	11·67	43·20	0·68
Sulphate of lime . .	—	1·36	1·36	0·68	—
Sulphate of magnesia	—	trace	trace	4·20	—
Chloride of sodium .	28·69	11·40	44·80	18·30	88·70
Iodide of sodium .	0·63	—	—	—	—
Insoluble matter .	2·70	10·30	3·30	0·32	0·03
Moisture	—	7·50	2·50	6·00	3·50
	100·00	100·00	100·00	100·55	99·83

A sample from Chili, analysed by Hochstetter, was found to contain 94·3 per cent. of nitrate of soda, the remainder being composed of 2·0 chloride of sodium, 0·2 sulphate of potash, 0·4 nitrate of potash, 0·9 nitrate of magnesia, 2·0 water, and 0·2 insoluble matter.

Manufacture of Nitrate of Soda from Caliche.—The nitrate grounds are on the edges of the Salares and rising ground; at La Noria, water is within a foot of the salar. There are some nitrate grounds without any apparent salar, and where the water is now at a depth of thirty to forty yards, or even more; but chloride of sodium must have been there originally to form the nitrate.

The nitre ground having been chosen, habitations are built of salt from the salar, wells are dug, boilers, settling tubs, crystallizers, and tubs for mother-liquor are fixed, and a stock of provisions is laid in for the people and the animals. The *salitero* or refiner can now commence operations, having, however, previously obtained his estacas or allotment of 200 square yards. Some manage to become possessors of very large tracts of nitre grounds. The salitero now directs his quarry-man to make openings with a heavy iron bar, increasing in width at bottom, through the costra and caliche to the coba; this is the *tasa* or cup, into which is put from one to fifteen hundred weight of very rough powder (made from nitrate of soda, and sulphur from the volcano of Isluga), the upper part being well rammed with loose earth; these are called "bombones," and are exploded, which loosens the earth, and turns it up. The irregular masses of caliche are broken into large lumps, collected

out of the loose mass and conveyed in panniers by asses to the officena or refinery; here the large pieces are broken into smaller and thrown into the boiler, to which, when nearly full, water is added, and the boiling commences, more caliche being added at intervals. In about seven or eight hours, the boiling point of the saturated liquid has attained a temperature of 240° F., when the mother-waters are added. The boiler-man now removes with a shovel the *borra* or salt, which has been precipitated together with earthy matters which have separated and subsided to the bottom of the boiler. The solution is bucketed out into the settling tube, where a further quantity of earthy matter, the *Ripia*, goes down, leaving a clear solution, which is then run into coolers, where crystallization takes place, producing *salitre* or refined nitrate of soda, which is shovelled out of the *bateas*, and dried by the sun's heat. It is now bagged and sent to the coast for shipment.

The best refined nitrate has been found to contain water, 0·11; salt, 1·84; sulphate of soda, 0·35; nitrate of soda, 97·70 = 100·00.

The nitre trade employs nearly all the people in the province, about 12,000, exclusive of foreigners and Chinese labourers. The exports are now 61,000 tons annually, and could be increased to any extent, as the nitrate grounds are inexhaustible. There are about forty nitre works and nine shipping ports, including Iquique. Messrs. George Smith and Co. have been using large boilers, and of more scientific construction, with advantage; they also have commenced boiling by steam. The fuel used is the tamarugo and algarobotrus; these are getting very scarce; hence much English and Chili coal is also employed.

This nitrate of soda has been known about a century. It was discovered by a woodcutter named Negreros, in the Pampa de Tamargal. Having made a fire at the spot, which still preserves his name, he found that the ground began to melt and run like a stream; the melted substance was afterwards examined and found to be nitrate of soda. In 1820, some of the nitrate of soda was sent to England; but, the duty being high, it was thrown overboard. In 1827, efforts were unsuccessfully made by an English house to export it. In 1830, a cargo was sent to the United States, and found to be unsaleable: a part was taken to Liverpool, but did not sell. A cargo was taken to France, and, in 1831, another to England, where it sold for thirty and

forty shillings the ton. The price has varied; in 1851 it was at fifteen shillings. Between 1830 and 1850, the quantity exported was 239,860 tons.

The following table exhibits the quantities more in detail.

Exports of Nitrate of Soda from Peru, in Quintals.

1830 . . .	18,700	1845 . . .	376,239
1831 . . .	40,385	1846 . . .	390,148
1832 . . .	52,500	1847 . . .	383,097
1833 . . .	92,700	1848 . . .	385,089
1834 . . .	147,800	1849 . . .	430,102
1835 . . .	140,399	1850 . . .	511,845
1836 . . .	158,534	1851 . . .	599,406
1837 . . .	165,369	1852 . . .	562,989
1838 . . .	129,610	1853 . . .	866,241
1839 . . .	149,576	1854 . . .	720,465
1840 . . .	227,362	1855 . . .	936,888
1841 . . .	278,488	1856 . . .	811,603
1842 . . .	359,918	1857 . . .	1095,833
1843 . . .	369,317	1858 . . .	1220,240
1844 . . .	380,191	1859 (1st half)	796,288

We subjoin also a table taken from the new edition of *Ure's Dictionary of Arts, Manufactures, and Mines*, of the trade of Great Britain in nitrate of soda in the year 1857.

Imports.			*Exports.*		
	Cwts.	£		Cwts.	£
Peru . . .	293,517	293,245	British West Indies .	6,691	6,691
United States .	25,408	24,467	Russia—Northern Ports	924	924
Hanse Towns .	24,775	24,763	Portugal	769	769
France . . .	7,971	8,701	Belgium	478	478
Other parts .	2,832	2,659	Spain	402	402
			Sweden	316	316
	354,503	355,836	Other countries . . .	790	790
				10,370	10,370

Imports of Nitrate of Soda into France.

1837—1846, average annual import, 2,319,605 kilogrammes.
1847—1856, „ „ „ 4,907,231 „

In the year 1857, the consumption of this salt in France amounted to 9,550,000 kil., the increase arising in great part from the rapid progress of the new process for preparing nitrate of potash from nitrate of soda.

NITRATE OF POTASH.

Ordinary saltpetre, nitrate of potash ($KO.NO^5$), sometimes called prismatic saltpetre, is likewise anhydrous in the crystallized state. The occurrence of this salt in the sap of the sunflower, of common borage, of the celandine, of tobacco, and other plants, as well as in small quantity in spring water, has not as yet been applied to any practical purpose.

Occurrence of Native Saltpetre.—Ready formed or native saltpetre has been frequently met with in the soil, and in several places it is extracted; it is never found, however, in distinct layers, like the cubic nitre in Peru, but disseminated throughout the soil, and occasionally as an incrustation upon the surface. Veins of nitrate of potash have, however, been found in a sandstone in Bradford County, Pennsylvania. (W. Ellet, Edinb. Phil. J. cvii. 367.)

In the chalk formation on the banks of the Seine, near Roche-Guyon and Mousseau, there are several caves, which are used as stables and for other purposes. In the front part of these caves, which look towards the south, but not in the hindermost internal parts, saltpetre is found in the surface rock; the matter containing the saltpetre is collected several times during the year, and is spontaneously reproduced; it is extracted in the usual manner. According to Lavoisier, the saltpetre is accompanied by chloride of sodium and chloride of calcium. He found in specimens taken from the cavern of Fouquières $3\frac{1}{8}$, from that collected near the church of Mousseau $5\frac{3}{8}$, and from another locality only $1\frac{1}{4}$ per cent. of nitrate of potash, after having treated the aqueous extract of the saline mixture with potashes.

The saltpetre caverns in the island of Ceylon, which were carefully examined by Davy, are extremely interesting. They consist of natural caves in a limestone rock containing magnesia and felspar, which have been gradually enlarged by the removal of the nitrified stone. Some of these, like that of Boulatwellegode, are the resort of innumerable bats, whose excrement collects in them. In others, there are none of these animals, as is the case on the cave of Memoora, which is situated in a hill about 300 feet

high, and thickly wooded; it is 100 feet broad, 80 feet high, and extends to the depth of 200 feet. The thickness of the roof is, therefore, not very considerable, and the floor is composed of the naked rock without any covering of earth. Davy found here sixteen workmen employed, each of whom furnished ½ cwt. of saltpetre yearly to the government. The fact, that this work has been going on, during the six dry months of every year, for the last fifty years, proves that the produce on the whole cannot be inconsiderable. Davy found, on examining a specimen of the rock from Memoora cave, in 100 parts,

2·4 nitrate of potash,	60·8 of residue, insoluble in
0·7 „ „ magnesia,	weak nitric acid, and
0·2 sulphate of magnesia,	consisting of felspar,
26·5 carbonate of lime,	quartz, mica, and
9·4 water, and	talc.

The potash is, no doubt, derived from the disintegrated felspar, and was always found accompanying the nitrates of the earths, whether these consisted of magnesia or of lime.

The mode of procuring saltpetre from these caves is simple and cheap, but somewhat crude. The workmen loosen the stone from the inner surface by means of iron tools, and mix the pounded mass with about an equal portion of wood-ashes. When water is poured upon the mixture, the nitrates of the earths part with their acid to the potash in the ashes, and the earths are precipitated, as carbonates of lime and magnesia. The clear decanted lye, which contains the nitre produced by the ashes, as well as that naturally present in the rock, is first exposed in pits and evaporated to a considerable extent by the heat of the sun alone; it is then further evaporated in pans to the point of crystallization. That which crystallizes on cooling, is crude saltpetre, which is immediately sent off.

Similar caves are known on the coasts of the Adriatic, in Italy, (Pulo di Mofetta,) in some parts of the United States, (Tennessee, Kentucky, on the Missouri and Crooked river,) in Africa, and in Teneriffe.

The mode of occurrence of native nitrates in South America, in some districts of India, Arabia, Egypt, Persia, Spain, and Hungary, is somewhat different. In India, Bengal and the neighbourhood of Patna are the localities whence the largest portion of the saltpetre comes, which is supplied to the European market from Houghly, having been previously boiled at Chiopera.

In Hungary, the country about Semeny, Debreczin, and Nagy-Kallo is celebrated for its saltpetre pits, and supplies the different saltpetre works in the counties of Bihar, Szaboltsch, and Szathmar (belonging to the Freiherr von Vaj), as well as those of Parndorf and Zorndorf in the County Wieselberg, Norod and Bürüs in the County Schaumeg, Szelnitz in Liptau County, Neusohl in the Gespannschaft of Sohl, and Oedenberg and Raboth, in the County Oedenberg.

These salts are found widely disseminated in the above-mentioned districts, but do not extend to any great depth below the surface, never lower indeed than where the air can easily penetrate. The infiltration of rain and dew naturally dissolves the salts, so that the soil is never moistened by pure water, but by a weak solution of nitre. When this solution is evaporated by the action of the sun and air, its place is immediately occupied by a fresh solution from below, which rises in consequence of the porous nature of the soil, in obedience to the law of capillary attraction, and is vaporized in the same manner. Thus all the saltpetre is gradually brought to the surface from the lower layers, and remains, after the evaporation of the water in hot weather, as an incrustation of considerable thickness, sometimes in the form of solid crystals, sometimes in bundles of fine threads. It is collected in the form of a saline mass mixed with earth.

Davy found in Bengalese saltpetre earth, from the district Tirhoot:

8·3	nitrate of potash,
3·7	„ „ lime,
0·8	sulphate of lime,
0·2	chloride of sodium,
35·0	carbonate of lime with traces of magnesia,
12·0	water in which was some organic matter, and
40·0	matter insoluble in nitric acid.
100·0	

The process to which this earth is subjected, is the same in principle as that practised with the rock of the caverns, only the addition of ashes is frequently omitted, from a scarcity of that substance; indeed, it is here not so essential, as the earth itself is richer in nitrate of potash. Nitrate of lime then remains in the mother-liquor, and is lost. The Hungarians treat the earth in precisely the same manner, after it has been loosened by the

plough and collected. This country (Hungary), as already remarked, is particularly abundant in saltpetre, which occurs mostly in boggy places; for example, in the old bed of the Theiss, on the left shore of the river, which is exposed to inundation; in the neighbourhood of certain salt-water bogs, and in other places. 100 square fathoms Hessian produce yearly 4¼ cwts.* of impure saltpetre, the produce being collected at six different times.

The soil in some parts of Spain is also incrusted with saltpetre, in New Castile, Arragon, Catalonia, La Mancha, Granada, &c., the produce of those districts being worked, according to Proust, at Saragossa, Alcazar de San Juan, Tremblaque, &c.

Formation of Saltpetre in the Temperate Zones.—From the preceding facts and observations, it appears that the localities which naturally afford saltpetre, without the intervention of man or animals, are situated chiefly within the tropics. The soil of those countries produces, without any extraneous assistance, abundance of nitrates for home consumption, and partly supplies the foreign market; but in the temperate zones the formation of potash-saltpetre, which is the most valuable, occurs only in a few spots, where its formation has not been assisted by the addition of ready-formed nitrates; and the natural produce of these regions is as nothing compared with the vast consumption of the salt. Nevertheless, a kind of artificial nitrification is always going on here upon a large scale, under certain other conditions, which are found combined only in the neighbourhood of inhabited places. The first among these, is the necessity of the presence of nitrogenized matter, either of vegetable origin, or consisting of the refuse of animal bodies or fluids, urine, excrement, blood, &c. &c., which, in the presence of powerful bases, such as potash, lime, magnesia, decay and rot, and gradually give rise to nitrates of the bases. Nitrate of potash, however, is found only in small proportion as compared with the nitrates of the earths, potash being contained in all soils to a much smaller extent than the earths.

All the observations and experiments which have been made, tend to show, that in the formation of saltpetre, the following conditions must always be fulfilled: namely,

The presence of the above-mentioned *bases*, lime, magnesia, potash, and these must be in a loose porous state, so as to be

* Jahrb. der k. k. geolog. Reichsanstalt 1850, pp. 324, 453.

easily permeable—as they are contained, for instance, in marl, chalk, mortar, &c., but not in the form of marble, dolomite, felspar, &c.

The presence of moisture in such quantity that the matters necessary in the formation of saltpetre may be uniformly penetrated, but not surcharged with the water.

A temperature of 15° (59° F.), *or* 20° (68° F.); a temperature of 0° (32° F.) is sufficient to put an entire stop to the process. Lastly,

The unimpeded access of air.

These conditions are universally necessary; but the colder regions require in addition—

The presence of decaying vegetable or animal matters, containing nitrogen.

The action of *light* appears rather to accelerate the process than to be absolutely necessary.

It is of little consequence, as will be easily conceived, to the formation of saltpetre, whether these conditions are of accidental occurrence, or whether they are expressly created for the purpose. In fact, the crude material for the production of saltpetre is as easily obtained in the temperate zones by artificial means, as by collecting the substances in which it has been naturally formed. The localities in which saltpetre-earth is artificially produced, are called *saltpetre plantations;* the earth, on the contrary, which is collected together from different places, is called *swept saltpetre.* (*Kehrsalpeter, Gayerde, Gaysaltpeter.*)

A few examples will indicate the manner in which advantage is taken of the different localities.

Saltpetre from Walls.—In densely populated towns, with narrow streets, where the excrements of beasts of burden, the refuse from slaughter-houses and trades of a like nature, the water from the houses, and the refuse of markets and other similar matters mix with the fluid in the drains, and are in a constant state of putrefaction, it may be seen, how the coating of mortar at the base of the external walls is gradually eaten away, and becomes covered with a flocculent, white, crystalline efflorescence,—this phenomenon is a source of alarm on account of the injury which ensues to the buildings, and is called *saltpetre rot.*

The same phenomenon is not unfrequent in other parts of the walls which are directly exposed, not to the mud of the streets,

but to the infiltration of fluids, for instance, from the drains of privies, or to the urine of cattle in stables.* It is, however, very necessary, before collecting any such efflorescence, to ascertain, either by the taste, or better by lixiviation and evaporation, the nature of the salt; for the observations of Kuhlman have proved, that these often arise from the sulphates and carbonates of the alkalies contained in the limestone, and do not consist of nitrates.

Production of Saltpetre in Switzerland.—The earth below the flooring of stables, or in the neighbourhood of dung-heaps, in the cellars of dwelling-houses, where the remains of vegetable or other organic matters have been left to decompose, is a material which may be used for the production of saltpetre. Thus, in Switzerland, for instance, in Appenzell, the position of the stalls on the declivities of the mountains, when not too dry, and having a northerly aspect, is made subservient to the production of saltpetre. When the building has its entrance towards the mountain, and the opposite side is supported by beams or a raised foundation, the floor of the stall is necessarily hollow. A pit is then dug two or three feet below the floor, and of the same dimensions, and this is filled with a sandy porous earth, which retains all the urine that falls through. In two or three years, this earth becomes sufficiently impregnated with saltpetre for lixiviation, and the same operation may then be repeated every year; for the saltpetre boilers affirm, that the earth which has already served for one saturation is, when again brought into the pit, better fitted than fresh earth for a renewal of the process.

Longpont.—The foregoing plan may be regarded as a crude saltpetre plantation, as is also that at Longpont, in France, where the stone quarry, which originated with the erection of the Abbey Church in that town, is employed for the same purpose. The quarry is sufficiently exposed to the air, and is always very damp. Earth and dung are alternately arranged in layers 4 inches thick, one above the other, and the whole heap is then covered with earth. Moisture being always present in sufficient quantity, it is not necessary to water it, but the liquid manure from the stables and houses is conveyed to it, and materially increases the amount of nitrogenized matter. At the expiration of the second year, the heap has rotted away to a uniform mass

* Nisbet has shown that nitrates are always present in stable-yard manure.

of earth, and must then be advanced near to the mouth of the quarry (more exposed to the air), where it is occasionally turned over, and in the course of two more years is in a fit state for lixiviating. From the dung of twenty-five cows, asses, and mules, about 10 or 12 cwts. of saltpetre are thus obtained.

Thouvenel's method.—A proposal, depending upon the same principles, was made seventy years ago by Thouvenel, and recommended by experienced men as quite compatible with the system of French agriculture. The proposal was, to connect the production of saltpetre with the sheepfolds, and use a portion of the manure from the sheep for that purpose. Whether agriculture does not suffer as much from deterioration of the quality of manure, as is gained by the production of saltpetre, still requires a positive and direct answer. The earth in the stalls and sheep-cots is, in the first place, loosened to about a foot below the surface, and the animals are plentifully supplied with straw. Whilst the dung of the sheep gradually forms manure with the straw, the porous earth absorbs the fluid excrement without mixing with the former. After some months, therefore, when it has become necessary, the straw manure may be removed, and the earth below it turned over and covered with a fresh layer of earth, which increases its power of absorption. This operation is repeated several times during the year, and the earth then becomes sufficiently impregnated with the excrementitious substances to fit it for the production of saltpetre. The operation is then conducted in an airy shed, where the earth is heaped up 3 feet high into a kind of wall or dam, turned over once a month, and watered at intervals with liquid manure. At the end of two years it is fit for extracting.

Sweden.—In Sweden, saltpetre is one of the revenue taxes, and is consequently prepared by the peasants on the estates themselves in wooden sheds or huts, the floors of which are covered with clay or boards. A mixture of loose earth, refuse of all kinds, both animal and vegetable, with lime, marl, or exhausted ashes, is made up into a heap, and watered from time to time with the urine of animals, partly to keep the mass damp, and partly to increase the quantity of saltpetre: for no animal fluid is so rich in nitrogen as urine. During the summer, the heap is turned over weekly, and in the winter every month, care being taken to keep the whole as loose as possible, either by the insertion of twigs, or by piercing holes through it. It is also

believed that saltpetre is more readily formed when the light is excluded. The whole operation requires two or three years.

Saltpetre Plantations.—The preparation of the so-called saltpetre earth, and the actual production of saltpetre upon a large scale, form two distinct operations in the *saltpetre plantations*, as is also the case in Thouvenel's method. Earth impregnated with putrid nitrogenized matter is either collected from cattle-stalls or slaughter-houses in the neighbourhood, or heaps in which prutrefaction can go on, are made for the purpose of producing this earth. There are three classes of substances which may be used for this purpose; the substance must either consist of vegetable matter, as weeds (belonging chiefly to the families of the *Solanaceæ*, *Euphorbiacæ*, or *Fungi*, which are those containing the largest quantity of nitrogen), pea, bean, and Indian corn-straw, sunflower, &c.; or of solid animal refuse, as the dung of birds and quadrupeds, the mud from stagnant ponds, mud from the streets, flesh, cuttings from the tanners, &c.; or lastly, fluids containing nitrogen, as urine, liquid from cesspools, water in which bloody flesh or cheese has been washed, &c. The vegetable substances are first spread out upon a layer of earth, upon these the other solid matters are laid to a height of some feet, and the whole is covered with a second layer of earth. The liquids are used for watering the heap, which must always be moistened throughout, but never wet. To allow the liquid to penetrate, holes are bored from above towards the middle. After a time, the separate fragments lose all form, and rot into a uniform mass, which is then mixed up with the earth below. It is certain, that during the putrefaction which goes on in such a heap, a very large portion of the nitrogen escapes as ammonia, which must be considered as so much loss of saltpetre; for ammonia is in all probability the starting point of the entire process of nitrification.

The earth thus prepared, must be intimately mixed with old mortar, marl, loose limestone, or lime ashes (the requisite bases), and exposed to the action of the air in a constantly moist state. Hence arises the necessity of giving the whole a great extent of surface, and forming it into heaps, as it must not be allowed to occupy too much space. When the height of the heap is more than a fathom, the upper part dries too rapidly, and the erection of the heap becomes too laborious; the shape of the heap must therefore vary, according to circumstances. When no roof protects the heap from the access of rain, the nature and inclination of

the ground must admit of the water which runs off being collected in a cistern or pit. The ground should, therefore, be a layer of clay, and the heaps should be opposed to the prevailing wind, and secured from inundation, by their position. Experience has also shown that a degree of moisture corresponding with that of ordinary garden mould, is most advantageous. The heap is generally made in the shape of a flattened pyramid, from 6 to 7 feet in thickness, and about a fathom high; a passage being left open at every 15 feet; a space must also be left between the heaps for the passage of the barrows used in building and removing them. The inclined surface of the pyramidal heaps is generally arched, but in such a manner that the arch is not so wide as the heap is broad. The spaces on each side are traversed by gutters, where the liquid used for moistening the heaps, which is kept in reservoirs, collects, so that it runs off and permeates the sides of the heap, just where evaporation is most rapid, and the formation of saltpetre chiefly takes place.

The following description of a covered saltpetre plantation is given by Boussingault.*

Fig. 124 is a perspective view of a shed enclosing the plantation; Fig. 125 is a longitudinal section of the same; Fig. 126 a transverse section; and Fig. 127 a plan.

The shed is about 30 feet wide, and of any convenient length, say 100 feet. The roof may be covered with thatch, tiles, or slate; but a thatched roof is to be preferred, as it affords a better circulation of air, and more efficient protection against heat in summer and frost in winter. The sides should if possible face north-east and south-west; they are closed with rough hurdles to protect the plantation from violent winds, the hurdles being covered inside with straw mats, which may be raised and lowered to regulate the draught, and to afford protection against sun and rain. The spaces above the doors are likewise closed with hurdles.

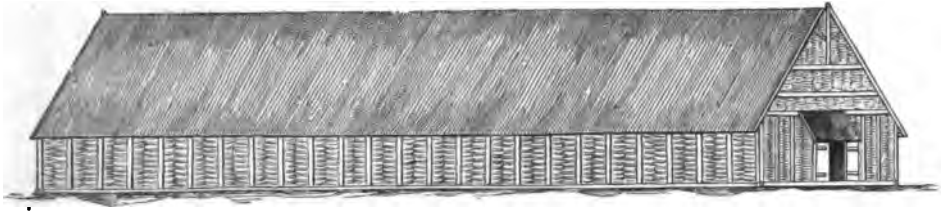
The ground within the shed is dug out to a depth of 2 feet; if the soil is argillaceous, it will be sufficient to ram it well throughout, but if porous, it must be dug out 6 inches deeper, and this space filled up with clay, so as to form a stratum impervious to moisture. A ditch, 2 or 3 feet deep, is also dug round the shed with sufficient inclination to drain off the surplus water.

The shed having been constructed, the excavation, 2 feet deep,

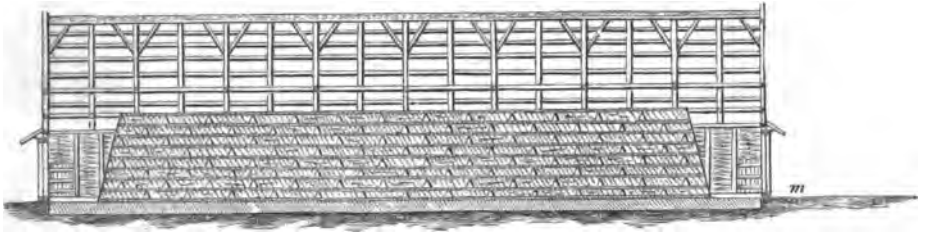
* Agronomie, Chimie Agricole, et Physiologie, par M. Boussingault, 2nd ed. 1861, ii. 24.

FIG.

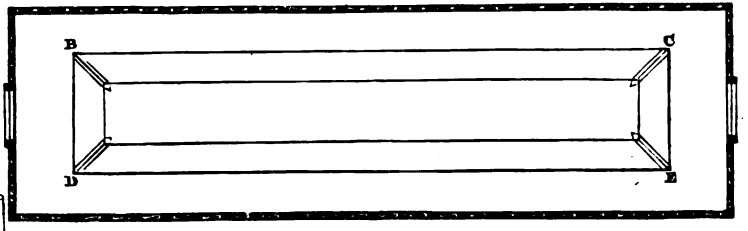
124.



125.



127.



130.

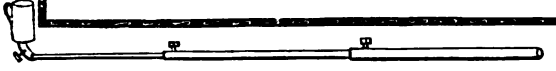
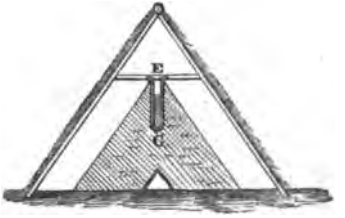
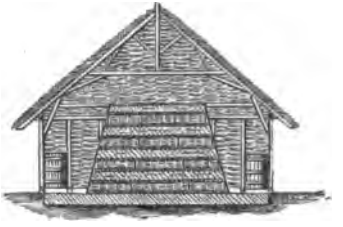


FIG.

131.



126.



128.

129.

is filled with earth prepared as above described. A rectangular space, B C E D (Fig. 127), is then marked out on the floor, 88 feet long and 18 feet wide, so as to leave a space of 6 feet all round. At each of the corners, B, C, D, E, and at intervals along the sides, B C, D E, stakes are fixed, rising 10 or 12 feet above the ground, and inclined inwards, so as to support the heap of earth to be afterwards built up.

A number of hurdles (Figs. 128, 129), 18 feet long, and of triangular section, each side of the triangle being about a foot long, are next placed on the floor, extending across the rectangle: the ends of them are seen in Fig. 125. The prepared earth is filled in between these hurdles, and to about 18 inches above them; another row of hurdles is then laid on the top, in the spaces between the lowest row, and covered with earth in like manner; a third layer is formed upon this, and so on till the heap has attained a height of 10 or 12 feet (Figs. 125, 126), each layer being, however, made somewhat narrower than the one below it, so as to give to the transverse section the form of a trapezium, 18 feet wide at bottom and 12 feet at top (Fig. 126). The inclination of the sides must, however, be varied according to the nature of the materials, earth of little tenacity, of course, requiring a greater inclination. The solidity of the heap may be increased by placing at the bottom of each layer a small quantity of straw, twigs, old rotten hurdles, &c. It is also advantageous to mix a certain quantity of straw or fresh stable manure throughout the heap, as small channels are thereby formed, which greatly facilitate the penetration of liquids.

If the construction of the hurdles should be found too costly, their place may be supplied by small faggots, placed end to end, and distributed through the heap in the same places as the hurdles: this arrangement, however, as we shall presently see, is less convenient for watering.

It is of great importance to have a good store of liquid for watering the heap. The best liquid for this purpose is urine; in default of this, the water which drains from dung-hills, the drainage of towns, and waste soap-suds, may be used: the last have the advantage of containing animal matter in a state bordering on putrefaction, and likewise an alkaline base to unite with the nitric acid. It is better to water frequently than to give a copious watering at once, and the heap should be kept moderately damp, but never wet.

When the heap is built up with hurdles in the manner above described, the watering may be conveniently performed with a copper funnel (Fig. 130), capable of holding about 2 quarts of liquid, having a tube 7 feet long, and provided with a stopcock, D, at the bend. The tube of this funnel is introduced into one of the hurdles as far as it will go, and the cock D being closed, three or four pints of liquid are poured in, the quantity being measured by marks on the side. The cock is then opened, and the tube slowly withdrawn, so as to diffuse the liquid equally throughout the layer. The same operation is repeated with each hurdle, excepting in the first row, or perhaps the first and second, from the bottom. The tube of the funnel being 7 feet long, conveys the liquid to the middle of the heap, and by repeating the operation on the other side, the whole will be watered. The upper surface is watered in the ordinary way with a watering pot. The space of 6 feet left between the heap and the side of the shed, enables the funnel to be withdrawn without difficulty.

When faggots are used instead of hurdles for supporting the layers of earth, the heap must not be raised above 6 or 7 feet, and the liquid must be poured on it with watering pots.

The ground on which the saltpetre plantation is formed should have sufficient inclination to afford good drainage; it should be near a good supply of water, but so situated as never to be exposed to inundation. A number of sheds, such as those above described, may of course be constructed on the same ground, according to the space: five or six, of the dimensions above given, will furnish employment for four workmen, three of them being occupied with making up the heaps, watering them, and lixiviating the ripe earth, and the fourth with the boiling of the lye, as will be presently described.

A plantation managed as above, yields, in the course of two years, from 120,000 cubic feet, or about 456,000 kilogrammes, of material—4500 kilogrammes of crude saltpetre, or 5 grammes per kilogramme.

In Sweden, the earth is made up into triangular heaps, and the whole is covered with a thatched roof, as represented in Fig. 131.

A very ingenious method of watering such heaps has been invented by M. le Baron de Chaumont, of Tourraine. A number of large cylindrical pots, E G (Fig. 131), of porous earthenware, 6 or 8 inches in diameter, and 3 or 4 feet deep, are sunk in the heap to within an inch of their mouths; the liquid is then poured

in, and gradually penetrating the pores of the earthenware, diffuses itself throughout the mass.

When the process of nitrification has reached a certain point, a white mouldy appearance is perceived on the surface of the heap, consisting of nitrates of the earths. The earth is considered fit or ripe for lixiviation, when 1000 cubic inches will produce about 5 ounces of saltpetre, a state which it generally requires three years to attain. For every 10 cwt. yearly produce, 120 cubic fathoms at least of earth must be laid out in heaps, of which one-third becomes ripe each year. Although no accurate method is known of ascertaining the quantity contained in the earth, except that of dissolving out a few cubic feet, the workmen are, nevertheless, enabled to judge of its fitness by the degree of cooling taste produced by the earth on the tongue. This method must obviously be subject to grave errors, the saltpetre being much too unequally distributed over the whole heap to admit of its quantity being ascertained by a single handful.

When the fitness of the earth has been proved by one or the other method, it is of importance, in order to save time and labour, that the bulk of earth in which the saltpetre has been produced, and which has to be lixiviated, should be reduced as much as possible, and this can only be done by accumulating the nitrates in one part of the earth. The application of the principle, which was explained with reference to the efflorescence of saltpetre on the soil in Bengal, affords a convenient means of doing this. The following is the method practised. When the earth is nearly ripe, no more liquid manure is poured upon the heap, as time would not be allowed for the nitrogenous matters to be converted into saltpetre, and these would only contaminate that which has already been formed. Thus no compensation is made for the liquid, which, leaving its saltpetre behind, evaporates from the surface above, but the liquid present in the heap is constantly drawn up by capillary attraction, and evaporates in the same way as before. In this manner the saltpetre is accumulated to a certain extent in the outermost layers, and is scraped off to a depth of 2 or 3 inches several times in the year. The earth thus collected cannot be used immediately, and is, therefore, best preserved under a shed, frequently turned over and sprinkled with water (not with manure), by which the amount of saltpetre is somewhat increased. At last but little remains of the whole

heap, and what does remain contains so little saltpetre, that it is not worth collecting, and the heap must be renewed. For this latter purpose, not only fresh earth is employed, but also that which has been lixiviated until it is exhausted and useless. It is also stated, that the earth still containing a little saltpetre, acts more powerfully in inciting the formation of fresh saltpetre than such as has been entirely deprived of that salt. In some places, the heap is simply reconstructed with its former dimensions upon and around the old residual portion, whilst in other parts it is considered better to mix this residue with the fresh earth and reconstruct the heap with the mixture.

The method adopted in Prussia with the saltpetre-earth is somewhat different from that above described, but in certain respects it is better adapted to the object in view; the heaps are there constructed with perpendicular sides, and are, therefore, very appropriately called "*walls.*" The side opposed to the wind is simple and flat; the opposite side forms a series of steps down to the bottom, which give greater firmness to the whole. On each ledge or step is a gutter which carries back to a cistern the excess of liquid poured upon it. In this arrangement, the watering takes places at the back, whilst the evaporation proceeds chiefly on the side opposed to the wind, so that the saltpetre is drawn by degrees towards the latter part, whence it is also gradually removed. Just as much lixiviated and fresh earth is added to the ledges behind, as ripe earth is removed from the front, so that the wall, retaining its form and thickness, is gradually being altered in position, but is always preserved at the same distance from the neighbouring walls. Thus, the production of saltpetre is never checked by the entire removal of the heaps, and this is a great advantage, as it is much more difficult to set the process going than to keep it constantly in action.

Theory of the Process of Nitrification.—When a general view is taken of the different methods of procuring saltpetre, it becomes evident that not one of them can actually be called an artificial production of the salt. Whatever bears this name in practice—as, for example, the cultivation of the "plantations"—is merely the combination and fulfilment of certain conditions, which have been found by experience to be absolutely necessary to that spontaneous process of a chemical nature which terminates

in the production of the nitrates. The work of those engaged in the plantations has no immediate influence upon this process, and only tends to ward off the obstructions which oppose it, and preserve the conditions which have already been enumerated.

These conditions have been ascertained, and established by numerous observations. Glauber, and at a subsequent period, Stahl (1698), occupied themselves with this subject; Lavoisier, in the year 1777, published his theory of the process in a pamphlet. In the year 1775, the French government offered a prize for the best treatise "upon the principles upon which the production of saltpetre is based, and the best method of putting them in practice," and the accepted and otherwise remarkable documents, amongst the sixty-six that were sent in, were made known by the Commissioners of the Academy, and enriched with explanations and remarks in a compendious treatise of their own: the knowledge thus gained, has been very much increased in more recent times by the important investigations of Kuhlmann, Liebig, Millon, Cloez, and Guignet.

The whole explanation of the process hinges upon the source of the elements of the nitric acid, and more particularly upon the source of the nitrogen.

Thouvenel, (to whom was awarded the prize offered, as above mentioned, by the Académie des Sciences, in 1776, for the solution of the problem of nitrification,) asserted that the formation of nitre depends upon the joint action of the air, of moisture, and of an organic substance in a state of putrefation. On exposing well-washed chalk to the action of air alone, he found that no saltpetre was formed in it, whereas the same chalk exposed in a basket over a vessel containing putrefying blood, was found to contain a considerable quantity of saltpetre.

In 1823, a discussion arose between Gay Lussac and Longchamp as to the source of the nitrogen in nitrification. Gay Lussac, relying upon Thouvenel's experiment, and others made by himself, maintained that saltpetre is never produced, excepting by the joint action of the air and an azotised organic body. Longchamp, on the other hand, attributed the formation of saltpetre in the nitre beds of India, Egypt, Spain, and La Roche-Guyon, in France, where the quantity of organic matter present appears insufficient to account for the result, to the direct combination of the elements of atmospheric air. The discussion, however, left the point undecided, and merely showed that new experiments

were required to ascertain the origin of the nitrogen. Since that time, numerous researches have been made on the subject, the result of which has been to show that nitric acid may be produced: 1. By the direct union of nitrogen and oxygen in presence of an alkaline or earthy base; 2. By the oxidation of ammonia; 3. By the oxidation of azotised organic bodies.

1. *Direct oxidation of Nitrogen.*—Cavendish showed, in 1784, that when electric sparks were passed for a long time through air in contact with water or an alkaline liquid, nitric acid is produced. The experiment, which may easily be repeated on a larger scale by means of a Ruhmkorff's coil, shows that the combination of atmospheric oxygen and nitrogen may be brought about by electric discharges taking place in the atmosphere; and as these discharges are very frequent in tropical regions, it is quite possible that the large deposits of nitre found in those countries may derive their nitric acid, in part at least, from this source.

There are, however, other causes, perhaps, more efficacious, which may give rise to the formation of nitric acid from the atmospheric elements. Schönbein has shown that active oxygen, or ozone, unites directly with nitrogen (in presence of bases), forming nitric acid; and from the experiments of Cloez, it appears that nitric acid is formed when air is passed over porous bodies, even though the air may have previously been completely freed from ammoniacal vapours.

Lastly, nitrogen is frequently oxidised by what may be called *inductive action*, that is to say, in presence of another body which has a stronger tendency to unite with oxygen. Thus Lavoisier and Saussure showed that nitric acid is always formed when hydrogen burns in the air; Schönbein has found nitric acid in air which has been passed over moist phosphorus; Boussingault has shown that a small quantity of nitric acid is formed when carbon burns in the air, and he thinks it probable that a similar action may take place during the slow combustion of organic matter in the soil; lastly, Chevreul finds that nitric acid is produced when fatty bodies are burned in the air.

The oxidation of nitrogen in all these cases is analogous to the solution of certain metals in acids in presence of other metals more soluble than themselves; thus platinum, when alone, will not dissolve in nitric acid, but when alloyed with silver it becomes soluble; so likewise copper, which does not of itself

dissolve in sulphuric acid, is readily dissolved when alloyed with zinc and nickel (in German silver).

All these phenomena may be ascribed to a peculiar polar condition which elements assume when in connection with other elements at the moment of chemical change.* Adopting the language of the electro-chemical theory, we may suppose that nitrogen of itself does not unite directly with oxygen, because the electric polarities of these elements are not sufficiently opposed; but when hydrogen is likewise present, that element at once becomes strongly positive and imparts this condition to the nitrogen, which thus becomes capable of uniting with the oxygen. But whatever may be the cause of this phenomenon, the experiments above mentioned are sufficient to show that the direct oxidation of nitrogen is of frequent occurrence, and must therefore contribute, to a certain extent, to the formation of saltpetre.

2. *Oxidation of ammonia.*—The conversion of ammonia into nitric acid takes place under a great variety of circumstances, but the final result is always that which is represented by the equation

$$NH^3 + O^6 = H\,NO^6 \text{ or } 3HO.NO^5;$$

it is precisely analogous to the formation of phosphoric acid, H^3PO^8, by the combustion of phosphoretted hydrogen, PH^3.

Kuhlmann obtained nitric acid by passing a mixture of ammonia gas and oxygen over spongy platinum heated to 300° C. (572° F.), the effect being due, as in other similar cases, to the condensation of the gas within the pores of the metal. Now Saussure observed that farm-yard manure acts in some cases, like spongy platinum, in determining the combination of the oxygen and hydrogen; hence Liebig suggests that the dung may, in like manner, determine the oxidation of ammonia, and consequent production of nitric acid. Collard de Martigny and Dumas have shown that nitric acid is formed when a mixture of ammonia and air is passed over lime or potash heated to 100° C.

The oxidation of ammonia may also take place, like that of free nitrogen, by the inductive action above mentioned; thus Schönbein finds that nitric acid is formed when a mixture of oxygen and ammonia gas is passed over moist phosphorus; and Péligot has shown that, when finely divided copper, moistened with ammonia, is exposed to the air, a considerable quantity of

* See a Paper by Professor Brodie, "On the Condition of certain Elements at the moment of Chemical Change. Phil. Trans. 1850, Part ii. p. 759.

nitrate of ammonia is formed; lastly, it appears from the recent experiments of Millon that all bodies, simple or compound, which absorb oxygen in presence of ammonia, may in like manner determine its conversion into nitric acid.

Ammonia may also be directly converted into nitric acid by the action of oxidising agents, such as chromic acid, permanganic acid, peroxide of lead, peroxide of manganese, peroxide of barium, and, according to Liebig, of strongly heated sesquioxide of iron. The formation of nitre in the soil is perhaps often brought about by the agency of sesquioxide of iron, which indeed acts as a carrier of oxygen from the air to the ammonia, first giving up one-third of its oxygen to the ammonia, and being thereby reduced to protoxide, which then absorbs more oxygen from the air and transfers it to the ammonia: and thus there is a continuous oxidation of the ammonia.

Considering then the facility with which ammonia is converted into nitric acid, and the great variety of circumstances under which it results from the decomposition of organic matters, so that, in fact, it is always present in the air, there can be no doubt that this alkali plays an important part in the process of nitrification.

3. *Oxidation of Organic Compounds.*—Nitric acid may be produced by the direct oxidation of organic compounds without previous formation of ammonia. P. Thénard has shown that it is formed by the action of ozone on organic substance. Gelatin, heated with a mixture of sulphuric acid and peroxide of manganese, also yields nitric acid. The formation of oxidised compounds of nitrogen when azotised organic bodies are burned with oxide of copper, is a circumstance well known to every analyst; and lastly, Cloez and Guignet have shown that nearly all azotised organic compounds may be transformed into nitric acid by the action of permanganate of potash.

Of the three modes of formation of nitric acid above enumerated the oxidation of ammonia is that to which the production of the greater part of the saltpetre found in the soil must be attributed. The formation of saltpetre in places where organic remains are exceedingly scanty, as at La Roche Guyon, and in certain caverns of Ceylon, doubtless arises chiefly from the oxidation of atmospheric ammonia. The numerous dead bodies of animals and vegetables, in undergoing putrefaction, afford a constant supply of ammonia to the atmosphere, and on the other hand, the porous

rocks on the surface of the earth and vegetable mould absorb and condense this ammonia with avidity.

Since then ammonia is always present in the atmosphere, the question naturally arises, why is not saltpetre found at all parts of the surface of the earth, when the necessary bases are present for fixing the acid? The answer is, that the formation of nitric acid from ammonia does not take place unless certain conditions are fulfilled. On reviewing the several reactions enumerated at page 292, 293, it will be found that the oxidation of ammonia by atmospheric oxygen at ordinary temperatures does not take place unless some more oxidisable substance is likewise present to set up the action. The substances which act in this manner are chiefly organic bodies in a state of decay, and thus we see how it is that the presence of organic matter is, for the most part, an essential condition in the process of nitrification, and yet that this process may go on in situations where the quantity of organic matter present is insufficient to account for all the nitric acid formed. Another condition which may favour the production of nitric acid is, as already observed, the presence in the soil of a substance, like oxide of iron, which may act as a carrier of oxygen.

It is probable also that ammonia plays a double part in the formation of saltpetre, first undergoing oxidation, and then saturating the resulting nitric acid and forming nitrate of ammonia. This salt is found indeed in all the liquors obtained from saltpetre-earth, though the greater part of it must be decomposed, as soon as formed, by the alkaline or earthy carbonates present in the soil, the ammonia being thus set free as carbonate, and ready to unite with fresh portions of nitric acid.

Finally, it must not be forgotten that the occurrence of saltpetre may sometimes be the result of a process long since finished, and for this reason its formation in particular situations may appear inexplicable, because the conditions which gave rise to it have long ceased to exist.

Treatment of the ripe Saltpetre-earth.

The successive operations to which the ripe earth is submitted, are undertaken for the purpose of separating the nitrates from it, converting these into nitrate of potash, crystallizing, and purifying the product.

Lixiviation of the Earth.—The point which requires the greatest attention in dissolving out the nitrates, is the use of as

little water as possible (as this must afterwards be almost entirely evaporated, with a corresponding expense of fuel), so as to leave no more of the salt behind than is required for its after-application in the heap; this quantity should be about 1 or ½ per cent. Lye of 12 or 14 per cent. is generally considered fit for boiling. If the process of lixiviation is to be carried on with any degree of certainty, the operator must be furnished with instruments, which will indicate with sufficient accuracy at any moment, and with ease, the amount of saltpetre in the different lyes. For this purpose the saltpetre-hydrometer is used, the scale of which consists of a series of divisions indicating the depths to which the instrument will sink when immersed in an artificial solution of 1, 2, 3, 4, 5, &c., per cent. of saltpetre in water. Each degree, therefore, indicates 1 per cent. of saltpetre, at that temperature at which the instrument was graduated; the indications are very accurate in pure solutions, and sufficiently so in crude liquors, which is the name given to the first solution from the earth.

The material for lixiviation is placed in casks with double bottoms covered with straw, and furnished with cocks (like those used in the potash works; see *Potashes*); these are arranged in the same manner one above the other in three rows, with gutters connecting them with the sunken lye cisterns. The same quantity of water is passed through different casks containing earth until it has become fit for boiling, and the same quantity of earth is treated with fresh portions of water until it retains only ½ to 1 per cent. of saltpetre. The advantages of this method, which was described and particularly recommended for the manufacture of saltpetre in the year 1820, by the *Comité consultatif des poudres et saltpêtres de France*, will easily be perceived from the following observations. Suppose each cask filled with 6 cubic feet of earth, containing about 8 lbs. of saltpetre, and suppose further, that half the water poured upon it is each time retained, and that just enough water is always added to drench the earth nearly to its surface (3 cubic feet), then the process will be as follows, supposing each cask to be lixiviated four times, and sufficient time allowed for the water to dissolve all the saltpetre:

	Poured upon	There will remain	There are poured off
1st water = 3 C.F.	Cask A.	1½ C.F. containing 4 lbs.	1½ C.F. containing 4 lbs.
2d „ = 1½ „	„ A.	1½ „ „ 2 „	1½ „ „ 2 „

These make, together, 3 cubic feet containing 6 lbs., and are

poured upon a fresh cask *B*, in which there are also 8 lbs. of saltpetre. When this has been dissolved, $1\frac{1}{2}$ cubic feet will remain, and $1\frac{1}{2}$ cubic feet, containing $\frac{6+8}{2} = 7$ lbs., *i. e.* 14·9 per cent. of lye for boiling, will flow off. It follows that:

	Poured upon	Will leave	And there will flow off
3d water = $1\frac{1}{2}$ C.F.	Cask A.	$1\frac{1}{2}$ C.F. containing 1 lb.	$1\frac{1}{2}$ C.F. containing 1 lb.
„ „ = „ „	„ B.	$1\frac{1}{2}$ „ „ $\frac{1}{4}$ „	$1\frac{1}{2}$ „ „ 4 „
4th „ = „ „	„ A.	$1\frac{1}{2}$ „ „ $\frac{1}{2}$ „	$1\frac{1}{2}$ „ „ $\frac{1}{2}$ „
„ „ = „ „	„ B.	$1\frac{1}{2}$ „ „ $2\frac{1}{4}$ „	$1\frac{1}{2}$ „ „ $2\frac{1}{4}$ „

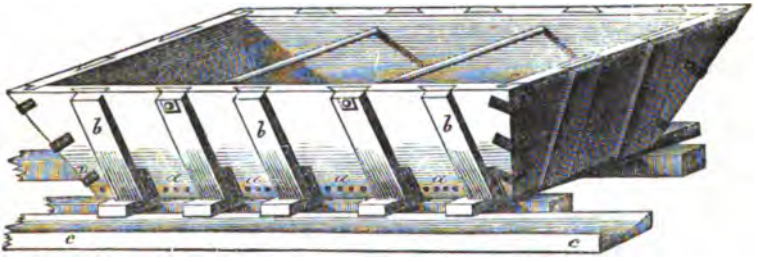
The 3d and 4th water together, after flowing from *B*, make 3 cubic feet, containing $\frac{8+4\frac{1}{2}}{2} = 6\frac{1}{4}$ lbs., and this is poured upon the cask *C*, where 8 lbs. are again to be taken up, so that $1\frac{1}{2}$ cubic feet of lye with $7\frac{1}{8}$ lbs. = 15 per cent. flow off for boiling, and as much remains of the same strength. In this manner, the operation proceeds without interruption; the first cask *A* being now exhausted to 1 per cent., is emptied and filled again. But when the same quantity of earth is to be exhausted to the same extent, *i. e.* to 1 per cent. at once, 800 cubic feet of water must be poured upon it, of which 795 cubic feet of lye containing 1 per cent. will flow off. In this case, therefore, 5 cubic feet of lye contain 1·6 lbs., and on the improved method they contain from $22\frac{1}{2}$ to 23 lbs., so that, in order to obtain 1 cwt. of saltpetre according to the improved plan $\frac{310 \text{ cubic feet}}{13{\cdot}8 \text{ cubic feet}} = 22\frac{1}{2}$ times less water have to be evaporated.

In a manufactory which produces yearly from 200 to 300 cwts. thirty-six casks are required, three rows of twelve each, so that the lye flows directly into the corresponding cask of the second row. Time must, of course, be allowed for the lye to dissolve the whole of the nitrates, and the cock is consequently kept shut during twelve hours. That the earth may be uniformly impregnated with the water, and no channels may be formed amongst the salt, all the coarser lumps, pieces of lime, &c, must be previously broken up; it is usual also to arrange the earth in the casks in the form of a funnel, and not with a flat surface, so that the water may flow through the middle, and effect a more complete solution. The water in the first operations flows from one cask to the other by itself, but when it has to be brought from the lowest row to the uppermost, a pump may be used to

economize time. The lixiviation of the ash is repeated three or four times according to the locality; but at every period of the operation, one cask is filled with fresh earth, while another contains earth once lixiviated, and a third, earth that has been twice treated with water. The lyes of different strength are distinguished by the appellations, *wash-water*, *weak*, *strong*, and *boiling lye*.

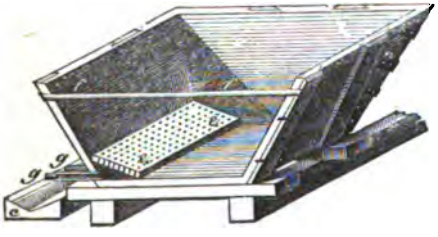
Lixiviating troughs, Fig. 131, may be substituted for the casks, and have the advantage of occupying less space; they are made of oak-wood in the form of a baker's trough, 16 feet long, half as wide at the upper part, and 4 feet deep. In one of the longer sides (the front one in the Fig. 132, towards which the bottom

FIG. 132.



slightly inclines) a number of holes, *a a a*, are bored between the stays, *b b b*, for the reception of tubes or cocks, to conduct the liquid into the groove, *c c*. To retain the earth, an inclined board pierced with holes, *e e*, Fig. 133, is placed in the interior, which is covered with straw or willow twigs. The iron rods, *f f*, are to prevent the sides from bulging, and the hoops, *n n*, keep the single boards together. The capacity of these troughs, each containing 218 cubic feet, is such that two are quite sufficient for the largest work. Water is poured upon the earth from several channels at the same time, into which it is pumped up, until it stands about 4 inches above the surface; at the expiration of twenty-four hours, the water is drawn off and a fresh supply added, until that which runs off contains only 1 per cent. of salt-

FIG. 133.



petre ; the trough is then re-filled. The charge in troughs of the above dimensions, calculated at 8 lbs. in 5 cubic feet, must contain altogether 256 lbs. of nitrate, which must produce a lye of about 10 per cent., with rather more than an equal bulk of water. The subsequent weaker lye is concentrated in the second trough, until it is fit for boiling. The exhausted earth is used in the construction of the heaps or walls, in the manner already explained.

The Crude Lye.—The lye for boiling, technically called *crude lye*, is, as the method of preparing it indicates, not only a solution of saltpetre, but contains all the soluble portion of the saltpetre earth, and its state of concentration must be regulated by the price of fuel. Besides the nitrates of potash (soda), lime, magnesia, and ammonia, it contains chloride of potassium, chloride of sodium, chloride of calcium, chloride of magnesium, carbonate of ammonia, and peculiar brown colouring matters of organic origin, which have not been examined, and which are usually classed together under the very indefinite term *extractive*. Thénard found in the dry residue of crude lye from the gypsum debris of Paris :

Nitrate of potash and chloride of potassium .	10
Nitrate of lime and magnesia	70
Chloride of sodium	15
Chlorides of calcium and magnesium . . .	5
	100

The presence of carbonate of ammonia is not surprising after what has been said with reference to the production of saltpetre. It explains what would otherwise be remarkable, viz., the absence of nitrate of alumina in the crude lye, for alumina is more abundant in the saltpetre-earth than any other base. The precipitation of magnesia is prevented by the salts of ammonia, and that of lime is at least retarded by the presence of nitrate of ammonia ; for no precipitate is produced when small quantities of carbonate of ammonia are added to a solution of nitrate of lime. The presence of nitrate of ammonia is explained by the observation of Kuhlmann, that carbonate of ammonia and nitrate of lime mutually decompose each other at a temperature of from 25° to 30° (77° to 86° F.) to form nitrate of ammonia and carbonate of lime. The brown colour of the lye is derived from the extractive matter, and the alkaline reaction from the carbonate of ammonia. It has frequently been asserted that there is more

nitrate of potash in the crude lye, than could have been produced from the potash present in the earth, that indeed potash itself has been produced. This may possibly not be an error, for by three years' exposure to the atmosphere, a perceptible quantity of the insoluble earth, which itself contains potash (grains of felspar, &c.), may have become disintegrated, and its potash would then unite with nitric acid, and be added to the whole amount of nitrate.

Treatment of the Lye.—All the nitrates in the crude lye have now to be converted into nitrate of potash. The salts of potash used for this purpose are either potashes, sulphate of potash, or chloride of potassium. The quantity of potash to be added, must, of course, be proportioned to the equivalents of the individual nitrates. It is chiefly for this reason that the plan of combining this process with that of lixiviation, by mixing the ashes with the earth previous to lixiviation, should be avoided: for we have no definite standard by which to regulate the addition of ash, and can only discover the proper quantity by the tedious method of testing a number of samples. The mixture is, therefore, best made with the crude lye, kept for that purpose in large cisterns with cocks for decanting, and decomposed by a solution of potashes in two parts of water, from another vessel. A small quantity is first tried, in order to ascertain how much of the potash solution is necessary, that is, until a precipitate is no longer produced with a certain portion of the lye; from this, the quantity required for the whole is easily calculated. As soon as the solution of potashes is introduced into the precipitating trough, and well stirred, a dense precipitate of carbonate of lime and magnesia falls to the bottom, while the nitrate of potash, with chloride of potassium and chloride of sodium, remains in solution. The proportion of chloride of potassium is much increased after this precipitation, for the decomposition is, of course, extended to the chlorides, as well as to the nitrates of the earths, at the expense of the chlorides of calcium and magnesium, for (if M represent 1 equivalent of calcium or magnesium), $MO.NO^5$ and $KO.CO^2$ become $KO.NO^5$ and $MO.CO^2$, and at the same time MCl and $KO.CO^2$ become $MO.CO^2$ and KCl. Now, as chloride of potassium is of much less value than potashes, that portion of the latter which decomposes the chloride of calcium and chloride of magnesium is so much loss to the manufacturer; for a smaller quantity of potashes cannot be used, as the decomposition of the

nitrates and chlorides of the earth is not consecutive but simultaneous. For this reason it is useless to calculate the necessary addition of potashes by the amount of nitrates only; and the nitrate of ammonia also requires an excess of carbonate of potash to decompose it. Neither is it advisable to concentrate the lye to 15 or 20 per cent., before adding the potashes, which is sometimes done, as that involves the necessity of repeatedly washing the precipitate, in order to remove the whole of the saltpetre. If, however, sulphate of potash is used, the lye must then be brought to this state of concentration. In this case, ($MO.NO^5$ and $KO.SO^3 = MO.SO^3$ and $KO.NO^5$,) sulphate of lime is produced, nearly the whole of which precipitates, and sulphate of magnesia remains in solution. To separate the sulphate of magnesia, a little excess of milk of lime may be added, when magnesia and sulphate of lime separate ($MgO.SO^3 + CaO = CaO.SO^3 + MgO$). The clear lye then contains saltpetre, chloride of sodium, and chloride of potassium, a small quantity of sulphate of lime being found in the colouring matters, almost entirely in the precipitate.

Chloride of potassium, which is obtained in large quantity during the purification of saltpetre, may also be used as an addition to the crude lye, when sulphate of soda can be obtained at a low price. According to Longchamp, the whole should be first treated with sulphate of soda; all the nitric acid of the crude lye then enters into combination with the soda, and sulphate of lime is precipitated. After milk of lime has been used to separate the magnesia, nitrate of potash and chloride of sodium can be obtained by the addition of chloride of potassium. The same object is attained in a more simple manner, after the separation of the magnesia by lime, when the clear lye is treated with a solution of chloride of potassium, and crystallized sulphate of soda in equivalent proportions (in the proportion of 1 : 2), which then produce the same effect as a mixture of common salt with sulphate of potash.

Whatever means may have been employed to decompose the crude lye, it must afterwards be allowed to stand until the precipitate has entirely subsided, and the clear liquors can be drawn off for boiling.

The Boiling.—The object of boiling is not only to concentrate the lye to the point of crystallization, but likewise to effect the separation of impurities. To understand the nature of the pro-

cess, the different degrees of solubility of the salts contained in the lye must be taken into consideration. Thus 100 parts of water dissolve:

At 0° C.	(32° F.)	—	7·5	parts of saltpetre.	(Gay-Lussac.)
„ 18°	(65° F.)	—	29·0	„ „	„
„ 45°	(113° F.)	—	74·6	„ „	„
„ 97°	(207° F.)	—	236·0	„ „	„
„ 100°	(212° F.)	—	400·0	„ „	(Riffault.)
„ 0°	(32° F.)	—	29·32	„ chloride of potassium.	(Gay-Luss.)
„ 11·8°	(53° F.)	—	34·5	„ „ „	(Kopp.)
„ 15·6°	(60° F.)	—	35·1	„ „ „	„
„ 17·5°	(64° F.)	—	33·3	„ „ „	„
„ 100°	(212° F.)	—	about 57·0	„ „	(Gay-Lussac.)

and of chloride of sodium about the same quantity (27 parts) at all temperatures. The solubility of nitrate of potash increases, therefore, to a much greater extent with the rise of temperature, than that of the chlorides; and the evaporation of water to a certain extent during boiling, is not attended by any deposition of saltpetre, as the loss of water is compensated by the rise of the temperature to 100° C. (212° F.). This increase of temperature, however, has but little influence on the solubility of the chlorides, which salt out and are separated during evaporation. We must remark, however, that the solubility of saltpetre is apparently increased by the presence of common salt.* This is explained by the fact, that these two salts cannot exist together in solution without mutual decomposition, so that the water in which they are dissolved really contains four salts, namely, chloride of sodium, nitrate of potash, chloride of potassium, and nitrate of soda; and the lye must consequently always contain some nitrate of soda, as common salt is never entirely absent; and in addition, chlorides, ammoniacal salts, lime, and magnesia in the state of bicarbonates, and likewise colouring matters, are generally found.

Fresh lye is constantly allowed to flow into the boiler, until its contents have attained the proper state of concentration. That

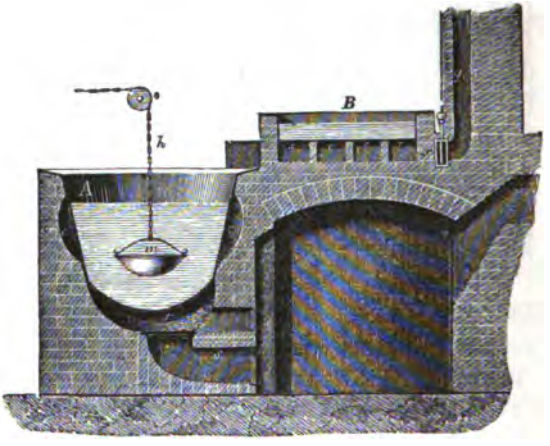
* A saturated solution of saltpetre (of 21·63 per cent., therefore), at 212° F., is enabled to dissolve, according to Longchamp, by the addition of—

5	10	20	25	parts of common salt.
0·75	1·27	1·83	2·58	parts more of saltpetre.

the temperature may not be lowered by each addition, the lye is previously warmed by the same fire in a separate pan.

Fig. 134 shows the manner in which the apparatus is arranged.

FIG. 134.



Access is obtained to the grate *r*, by the door *a*, and to the ash-pit *s*, at *b*. The flame first plays upon the bottom of the copper boiler *A*, and passes from thence through two walled apertures to the flues *c*, *c*, *c*, *c*. These, forming first a horizontal ring, heat the sides of the boiler, and extending upwards, pass under the bottom of the warming-vessel *B*, traverse the space below it several times, and then open into the chimney *g*, which is supplied with a damper *x*, for regulating the draught.

At the commencement, and throughout the time of boiling, a thick dirty scum rises to the surface of the liquids, which is removed from time to time, and emptied into the lixiviating vessels, that no loss of lye may occur. This impurity is derived from the organic matters in solution, which gradually coagulate, and become insoluble. The change which they undergo is caused partly by contact of air; and this explains why a less deeply coloured lye is obtained from earth which has been kept for some time, and not moistened during the latter period with excrementitious matter. Another effect produced during boiling, is the decomposition of a portion of the carbonates of the earths, which are precipitated as the carbonic acid holding them in solution is expelled, and these render the liquid turbid. This

decomposition is completed shortly before the lye is sufficiently concentrated. At the same time, when the evaporation has somewhat advanced, the difficultly soluble sulphate of lime begins to deposit as a crystalline powder. The phenomena are very similar to those which are observed in boiling salt brine, and a deposit would attach itself to the bottom of the vessels, as in the salt-pans, and give rise to the same difficulties, if a method of prevention were not adopted, which is applicable to all similar cases. When the earths begin to precipitate, a small flat vessel, *m*, is immersed, nearly to the bottom of the boiler, by means of the chain and pulley, *h, o*. While the great mass of the lye is boiling, and in violent motion, comparative rest exists in the interior of the vessel *m*, so that the particles in suspension, which are in constant agitation in the external fluid, can deposit in it without being again thrown out. The vessel *m* must be drawn out occasionally and emptied. The scum is allowed to drain into the evaporating pan from a box placed above it.

At a later period, when the concentration is more advanced, the chlorides of the alkali-metals (either common salt, or chloride of potassium, or both, according to the process adopted) are seen crystallizing on the surface in cubes, which then fall to the bottom. The fire should then be slackened, that larger crystals may form, which deposit more easily, and do not retain so much lye on removal. The same vessel *m* may be used for removing them, or as the crystals do not easily attach themselves to he pan, they may be scooped out with a colander. When the lye has attained the proper strength, which is the case when a drop placed on a cold plate soon becomes solid, a part of the chlorides has separated; but quite as much remains dissolved in the lye. The latter indicates 48° to 50° on the saltpetre hydrometer, and is left to stand for 15 to 18 hours, that it may become perfectly clear; it is then poured off into the copper crystallizing pans, where, at a temperature of about 50° (122° F.), the saltpetre crystallizes, as *crude saltpetre*, in small yellow crystals containing common salt and chloride of potassium. In those works where refined saltpetre is made at the same time, the crystallization is allowed to take place in the refining pans, and with the same precautions as if crude saltpetre were the only object of manufacture.

The mother-liquor, which contains either an excess of potash, or undecomposed nitrates, is added to the next boiling, until, by the

frequent repetition of the process, it remains in such excess, that it may be treated for the salts contained in it, or returned to the heaps with the earths which deposit in the vessel *m*. The chlorides which crystallize also contain much saltpetre, which must not be lost. The manner in which this salt is extracted is ingenious. A small willow basket, filled with the salt, is suspended in boiling water, another basket full is then substituted in the place of the first, and this is repeated with the whole quantity of salt. There must be much less water used than is requisite for the solution of the whole salt. At first, therefore, a saturated solution of the chlorides is produced, which takes from the second and following baskets no more of these, but all the saltpetre, so that, at last, the water employed contains the whole quantity of saltpetre, but only a small portion of the chlorides. This solution is added to the boiling lye, and the chlorides are used for other purposes.

Refining process.—The crude saltpetre contains no carbonates of the earths, but is contaminated with the extractive matter, and a considerable quantity of chloride of potassium and common salt, which, together, often amount to 25 per cent. These chlorides are the most difficult to remove of all the impurities, and are exceedingly objectionable in all the applications made of the saltpetre, whether for the preparation of aquafortis, in medicine, or more particularly for the manufacture of gunpowder, for which saltpetre must not contain more than $\frac{1}{1000}$th of chloride. The reasons are, therefore, obvious, which render a most complete and careful purification necessary. The best process, introduced by the French (Beaume and Lavoisier), is partly dependent upon the unequal action which heat exerts upon the solubility of saltpetre and of the chlorides, and partly upon the effect produced by animal gelatin (glue) upon the extractive matters, which (like tannin) form with it insoluble combinations: partly, however, upon an ingenious method of avoiding the chief cause of impurity in the crystals. It is well known, that in a fluid containing several salts on the point of crystallization, only homogeneous crystals, *i.e.*, such as consist of one salt alone, will be formed, except in those cases where the law of isomorphism admits of two salts taking part in the formation of one and the same crystal. Saltpetre, however, and the chlorides, do not come under this category, and consequently, crystals of saltpetre deposited from a solution of chloride of sodium (or chloride of potassium), will

contain none of the latter salt, but will only be contaminated by the mother liquor on their surface, from which, however, they can be freed without difficulty. Unfortunately, spaces are left in the larger masses of crystal, by the growth of new layers over the inequalities of those already formed, which remain filled with mother-liquor. It is in consequence of this that dry saltpetre, when pounded, gives a moist powder, these internal spaces being destroyed by pulverization, and the liquor then flowing out. In the refining process, this evil is avoided by purposely causing the formation of very small crystalline needles, which contain few or no pores.

The process is generally commenced in the evening, by dissolving a sufficient quantity of crude saltpetre in a roomy copper pan. Care is taken, at first, to add no more water than is requisite to dissolve the crude saltpetre at the boiling temperature, 1200 lbs. of water to 6000 lbs. of the crude salt. The result will be better understood by an example. Suppose the saltpetre to contain 6 per cent. of chloride of potassium and 14 per cent. of chloride of sodium; then the charge in the pan, without taking the other impurities into account, will contain:

		The 1200 lbs. of water are capable of dissolving at a temp. of 212°F.
Chloride of potassium . . .	360 lbs.	684 lbs.
Chloride of sodium	840 „	324 „
Saltpetre	4800 „	4800 „
	6000 „	

and there will remain, when the water has ceased to act, 840—324=516 lbs. of chloride of sodium, undissolved, whilst another portion, 324 lbs., will dissolve with the chloride of potassium and saltpetre. To save time, the whole of the water, and a portion of the saltpetre, are placed in a pan overnight, and in the morning, when the first portion has dissolved at a low temperature, the remainder is gradually added (about one-fifth at a time), and the heat increased. The scum, which during the stirring collects on the surface, is removed, and when the solution is effected, and the liquid has been boiled for some time, the chloride of sodium is scooped out from the bottom of the pan. The saturated solution would now deposit crystals during the following operation: for it must always be kept hot, and water conse-

quently be evaporated. Before proceeding further, therefore, the solution is diluted with 800 lbs. more water,* and again boiled, with the addition of 2 lbs. of glue to the boiling solution. The remaining extractive matter immediately separates with the glue, and rises to the top, whence it is removed. When scum has ceased to rise, the whole is allowed to stand till the following day. During this time, nothing must be allowed to crystallize, and the fire is consequently regulated, so as to produce as constant a temperature of 88° (190° F.) as possible. Before proceeding to crystallize, the suspended matter must be allowed to subside, that no portion of it may be mixed with the crystals. The transference of the liquid into the crystallizing pan, Figs. 135 and 136,

FIG. 135.

is therefore performed with the greatest care, and it is better to leave a portion of the lye behind than run the risk of contaminating the crystals. The pans are constructed of hammered copper, in the form of a flat three-sided prism, with the edge screwed firmly to a platform, *a*, of oak timber. The double inclination of the vessel, namely, the inclination throughout its whole length, and that of the bottom towards the centre, causes the deepest point to be at one of the narrow sides (at *n*): this is purposely so arranged. The lye requires six or seven hours to cool down to the temperature of the surrounding air; and then the formation of large crystals is prevented by constant stirring

FIG. 136.

* In most technical books—for instance, those of Dumas, Prechtl, Schubarth, &c., the addition of cold water is said to cause the precipitation of more chloride of sodium, in consequence of the reduction of temperature. This statement, which contains a palpable impossibility, is probably an oversight, if it is not the incorrect explanation of some phenomenon which occurs during the process.

and agitation; the saltpetre is obtained as a snow-white powder, consisting of fine crystalline needles—"*saltpetre flour.*" As this increases in quantity, it is drawn out of the lye by the workmen, towards the higher parts of the pan, where it remains until the (still coloured) lye, inasmuch as it is not kept back by capillarity, has drained away into the lower part. When the upper layers become whiter and less coloured, they are removed, with a colander, to the wash tub. About 1200 lbs. of mother-liquor remain. When the proportions above stated have been attended to, only traces of chlorides can accompany the saltpetre. Suppose the lye to cool down to 28° (65° F.), then in the above example, we shall have the following relations:

Dissolved altogether by the 12 cwts. of water.	The 1200 lbs. of the mother-liquor are capable of holding in solution at 18° (65° F.).	They will therefore crystallize
Saltpetre . . . . . 4800 lbs.	. . . 348 lbs.	. . . 4452 lbs. (flour)
Chloride of sodium . 324 „	. . . 318 „	. . . 6 „
Chloride of potassium 360 „	. . . 396 „	. . . 0 „

i.e., the flour will contain in this case, 0·1 per cent. of chloride of sodium, and the quantity of this substance, even in the most unfavourable circumstances, for instance, by excessive cooling, will never much exceed 1 per cent. But this quantity is almost entirely removed at the same time, when the mother-liquor is allowed to separate from the interstices of the flour, which mother-liquor will be so much the more impregnated with chloride, as the crystals themselves are freer from it. The process of *washing*, that is, the removal of the mother-liquor and the chlorides, is essentially the same as that called claying, or liquoring, in the sugar refineries. It consists in expelling the mother-liquor from the interstices of the crystalline powder, by means of a saturated solution of pure saltpetre. A solution of this kind can, of course, dissolve no more saltpetre, and therefore none of the fluid; but it dissolves the mother-liquor and the chlorides, with as much ease as pure water would dissolve them. When these impurities have been removed, the interstices between the crystals are filled with a solution of pure saltpetre, which, on drying, constitutes the whole mass. In transferring the fresh flour to the wash-pans, Figs. 137 and 138, it should be heaped up in some measure, as it shrinks considerably in washing. The washing tubs are 10 feet long, 4ft wide, and in other respects like the lixiviating cisterns, only they are provided

with a second pierced bottom, so that the fluid running off from the holes *a*, which are furnished with plugs, may be carried off by the gutter *d*. Each tub requires 144 lbs. of water, of which 60 lbs. are first poured with a watering-pot over the flour, and allowed to remain on the saltpetre, with closed plugs, for two or three hours. The whole of the chlorides are dissolved at the expiration of this time; the plugs are then removed, and the lye is allowed to trickle through during another hour. The operation is then repeated with the same quantity of water, and lastly, with the remaining 24 lbs. The first portion of water, and some of the second, contain the chlorides, besides saltpetre, and are allowed to flow into the crystallizing pans with the mother-liquor. The remainder, and the third portion of water, together 60 lbs.,

FIG. 137.

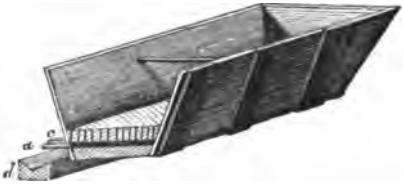
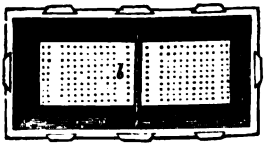


FIG. 138.



which contain nothing but saltpetre, are used instead of fresh water for the next portion. It is, consequently, only for the first operation that 144 parts of water are requisite; afterwards, the washing is commenced with the pure solution of saltpetre from the foregoing process, and finished with 84 lbs. of fresh water, nearly the whole of which is again obtained as a pure solution of saltpetre. The washed flour remains for some days in the wash-tub, and is then dried in a pan heated, very gently by the escaping smoke of the boiler, with constant agitation. The dry saltpetre must be sifted, to remove the lumps, before being sent into the market. On an average, 60 cwts. of the crude salt produce 35 to 36 cwts. of refined saltpetre, which is now fitted for all purposes, and particularly for the manufacture of gunpowder.

When sufficient mother-liquor has been collected, it is submitted to a separate treatment. It is evaporated with a constant addition to the boiler, as was the case with the crude lye, to two-thirds of its original bulk, the crystallizing common salt and skum are removed as before, and, at last, it is clarified with glue. It must be borne in mind, that this mother-liquor contains nitrates of the earths, besides the chlorides, and that the former will

have increased to such an extent, that it becomes necessary to decompose them by an addition of solution of potashes. When this has been done, the clear liquid is poured into the crystallizing pans, and the process repeated as before.

The older process of purification differs from the French method, in not producing any saltpetre-flour, but in submitting the crude salt to two successive crystallizations, each of which affords a cake of salt composed of large crystals. For the first crystallization, the same quantity of water is employed as in the French method, namely, one-fifth of the weight of the crude saltpetre, so that a portion of the chlorides remains undissolved. In the second recrystallization, the once purified salt is dissolved in one-third its weight of water, so that the residue of chlorides may remain dissolved. The second crop of crystals, after being dried, is considered sufficiently pure for commercial purposes. The use of glue was at first peculiar to this older process, but was afterwards adopted from it in the more recent method.

In Austria, milk of lime is added to the solution of the crude saltpetre in three-fifths water, to decompose the extractive matter, and the whole is crystallized without previously separating the deposit. A saline mass is obtained, from which the lowest impure layer is scraped off, and the mother-liquor drained away. Instead of recrystallizing this crude product, the whole is placed upon a substratum of wood-ashes covered with bibulous paper, which absorbs the residue of mother-liquor with avidity, provided care has been taken to prevent the mass from previously becoming too dry. The mass is left covered in this manner for fourteen days, when it is dried. It is hardly necessary to point out the inefficiency of this process.

In Sweden, where saltpetre is prepared on a small scale by individuals, the refining is not made a distinct process (see p. 327). The crude lye is boiled, until the greater part of the extractive matter and the chlorides have separated, and the concentrated liquor is treated, after having been strained, with as much water as will serve to hold in solution the chlorides which have not separated; the whole is then recrystallized. The production of saltpetre-flour, and the method of washing it, differ in no way from the plan already described. The washed flour is, however, melted in iron vessels in order to obtain a cake on cooling. In this state, the saltpetre is more easily conveyed to a

distance, as it occupies one-third less space, and the collector is enabled to judge, in some measure, of the purity of the salt by the appearance of the fractured surface. Pure saltpetre has, in the melted state, a coarsely fibrous structure, and is very translucent. The one-eightieth part of common salt can be detected in this manner; when one-fortieth is contained in the saltpetre, the nucleus is no longer fibrous, and if the common salt amount to one-thirtieth, the fibrous texture is perceptible only at the edges of the cake. As the great heat requisite to fuse saltpetre, and portions of carbon inadvertently falling into the fusing salt, always occasion partial decomposition, and give rise to the production of the deliquescent nitrite of potash, it is not desirable to fuse it, as it dissolves afterwards with difficulty, and is by no means easily pulverized.

Production of Nitrate of Potash from Chili Saltpetre.

Nitrate of soda is easily converted into nitrate of potash, by adding it to a hot concentrated solution of carbonate of potash. An immediate precipitation of carbonate of soda takes place, and if this be removed, as long as it continues to separate on further evaporation, and the remaining solution left to cool in the crystallizing pans, *saltpetre-flour* is obtained, which merely requires washing and drying as above described, to render it pure. 100 lbs. of nitrate of soda require, according to the purity of the salt, from 80 to 100 lbs. of carbonate of potash.

This mode of preparation is much easier than those already described, and in localities where potash is not too expensive, it is now extensively adopted.

The chief difficulty experienced in carrying it out, arises from the presence of common salt in Chili saltpetre; for if more potash be added than is required to decompose the nitrate of soda, the excess decomposes chloride of sodium to no purpose; and in the contrary case, the product is likely to be contaminated with undecomposed nitrate of soda. The best way of averting this inconvenience, is to purify the nitrate of soda by previous crystallization.

Some manufacturers render the potash caustic, by means of lime, before mixing it with the nitrate of soda, and after keeping the mixed solution in a state of ebullition for some time, leave it to cool slowly in a closed vessel. Nitrate of potash then crystallizes out, and caustic soda remains in solution. An additional

quantity of nitrate of potash may also be obtained from the mother-liquor by further evaporation. A patent for this process was taken out in 1850 (No. 13,231), by Benjamin Rotch, who also dries the crystals of nitre by means of a centrifugal machine.

Another patent for obtaining nitre in this manner, was granted to W. E. Newton, (1858, No. 1013), the process being conducted in the apparatus of which Figure 139 is a side elevation, and Figure 140 a plan. A is a vessel for slacking and decanting off the lime; it is provided with a valve at *a*, Fig. 138, and also with a pipe leading to the vessel D. B, Fig. 140, is a vessel in which the nitrate of soda is dissolved and allowed to settle; it is

FIG. 139.

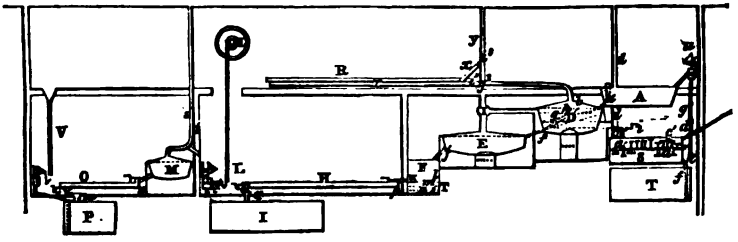
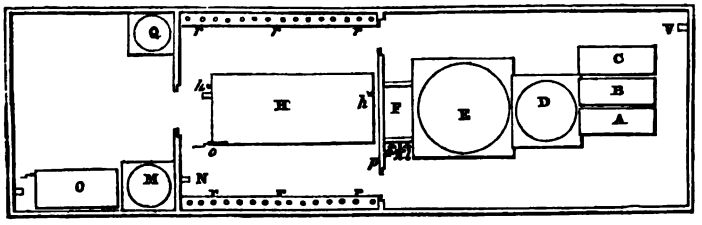


FIG. 140.



provided with a pipe leading to the evaporating boiler or vessel E. C, Fig. 140, is a vessel in which potash (of commerce) is placed, together with such a quantity of water as will not be sufficient to dissolve any considerable quantity of the neutral salts contained therein; a pipe similar to those above mentioned leads from this vessel C to the boiler D. The vessel C is not necessary when it is not required to obtain either saltpetre or caustic soda of great purity, and when this vessel is dispensed with, the potash is introduced directly into the caustifying boiler D, through the man-hole *b*, Fig. 139, which is provided with a

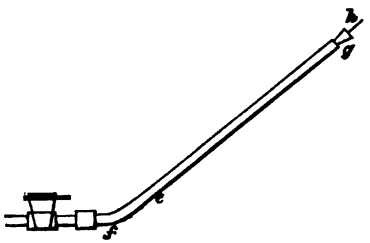
suitable trap or cover for that purpose. The boiler D is set over a furnace, and is also partially heated by a steam jacket leading from the boiler E. The pipe *c* conducts the water of condensation from this steam jacket into the washing apparatus S (Fig. 139), shown detached in transverse section in Fig. 141. The waste steam escapes by the steam pipe *d*, Fig. 139. The boiler D is provided with a cock or valve *e* of peculiar construction (shown detached and on an enlarged scale in Fig. 142), for the purpose of drawing off the clear lye into the vessel E, when a sufficient quantity of carbonate of lime has been deposited. This cock differs from ordinary cocks, but is similar to those in use in manufactories for decanting liquors from sediments. Its hinder part projects some distance into the interior of the boiler, and to the projecting part *f* a bent pipe is attached as shown in Fig. 142, in such a manner as to be capable of being set at any inclination, and thus present its open end *g* at any required distance from the surface of the contents of the vessel D, so that the open end of the pipe may be gradually lowered as the quantity of liquid contained in the vessel D diminishes. The open end *g* of this tube is provided with a stopper *h*, having a rod projecting above the surface of the liquid to prevent the entrance of any solid matters or sediment inside the tube.

FIG. 141.

FIG. 143.

FIG. 144.

FIG. 142.



The boiler D is also provided with a valve *i* (Fig. 139), for emptying the pasty contents into the washing apparatus S.

E is a boiler, also provided with a man-hole, and in which the clarified nitrate of soda and the clear potash lye, are evaporated to the degree required for obtaining by crystallization about five-sixths of the saltpetre produced by the reaction which takes place. This boiler communicates, by means of the cock *j*, with a rectangular vessel F, surrounded by masonry or brickwork, and having a double air valve at top. In this vessel the solution is allowed to remain until perfectly settled. A screw-valve *k*, fixed at a little distance above the bottom of this vessel F, serves to

draw off the liquor into the shallow crystallizing vessel H. The vessel F is provided, at its lower part, with another vessel G, which is separated from it, by means of a false bottom, and serves to receive the sediment through the cock *l* when its level approaches the cock or valve *k* above mentioned. This may be ascertained by drawing off every day, a few drops of the liquid through the small cock *m*, placed for that purpose, a little lower than the cock *k*, leading to the crystallizing vessel. The chamber G is provided with a cock *n* for drawing off its contents.

The crystallizing vessel H consists of a large shallow vessel with a flat bottom, and is provided with a moveable cover, and mounted upon trunnions *h''*, the one set a little lower than the other, so that the cock or valve situate at *o* shall always be at the lowest point when the vessel is tilted. This arrangement prevents the mother-liquor from remaining in the part *o p* when the crystallizing vessel is inclined, the mother-liquor being allowed to escape through the cock *o* and funnel *q* (Fig. 139), into the receptacle I, underneath.

The saltpetre, on being removed from the crystallizing vessel H, is left to drain in closed vessels J, having perforated bottoms (shown detached at Fig. 143), which are placed upon or over the openings or holes *r r*, Fig. 140. The saltpetre is to be treated several times with water, which will wash out the caustic soda lye. Beneath the openings *r r* is a waste pipe leading to the receptacle I. All the above-named vessels and parts are to be made of iron.

K, Fig. 144, is a copper pan for washing the saltpetre in the quantity of acidulated water necessary for neutralizing any free alkali contained in it; L is an apparatus for raising the saltpetre to the drying apparatus; M is a second evaporating vessel (of iron) for the concentration of the mother-liquors, which are raised, for that purpose, from the receptacle I by the pump N. This evaporating vessel is provided at *s*, with a cover and steam pipe, and also with a pipe *t*, for the escape of the condensed water. When the liquor is sufficiently concentrated, it is allowed to escape through the cock *u* into the crystallizing vessel O, which is mounted in the same way as the first large one H. The lye passes from the crystallizing vessel O, through the cock *v* and funnel *w*, into the receptacle P; Q (Fig. 140), is a small iron pan or boiler, for the evaporation of the lye; it is provided

also with a steam escape pipe and a pipe for the escape of the condensed water.

R (Fig. 139), is a drying apparatus composed of a large iron tray or trough with raised sides, under which circulates the steam from the boilers D and E, being conducted thereto by the pipe *x*, adapted for that purpose, to the main steam pipe *y*. By means of the valves 1, 2, 3, the steam may be directed either round the boiler D, or under the drying trough R, or out into the atmosphere through the opening *y*.

The washing apparatus S (represented in longitudinal section at Fig. 139, and detached in transverse section at Fig. 141), is composed of a vessel rounded at bottom, and in which is mounted a shaft *a'*, worked by means of a handle *b'*; upon this shaft are set a number of T-shaped beaters, *c' c' c'*, which serve to agitate the carbonate of lime in the washing water conducted thereto by means of the pipe *d'*, the carbonate of lime escaping through the waste-cock *e'* below.

T are the reservoirs for the washing water, to which it is supplied by means of bent or forked pipes *f'*, which are provided inside the washing apparatus, with decanting cocks similar to that above described. There are two of these reservoirs, one only of them being shown in the drawing, the other being situate behind it. They are intended to receive the water, alternately before it is supplied by the pump U to either of the vessels A, B, or C. The suction-pipe *g'* of the pump is forked, each branch being provided with a cock in order to supply one or other of the reservoirs as required. The supply pipe is also furnished with cocks in order to supply water to any of the vessels above where it may be required. In Fig. 139, V is an iron tube or funnel for conducting the saltpetre as it comes from the drying apparatus R into the barrels, or other suitable receptacles placed below for the purpose.

The following method is given by Gentele.*

An iron boiler, provided with a discharge pipe, is set in such a manner, that the fire shall only play on its sides. Another boiler is fixed above, also having a discharge pipe, which may be heated in the ordinary way, the arrangement being such, that the contents of the lower boiler may be run off by the discharge tube, into the crystallizing vessels.

* Dingler's Polytechnisches Journal, cxviii. 201.

The quantities of Chili saltpetre and potash employed are about equal, and every 100 lbs. of the former require 40 lbs. of water to dissolve it. Half this quantity of water is poured into the upper, and half into the lower boiler, the nitre is dissolved with aid of heat in the upper, and the potash in the lower vessel. As soon as both liquids boil, the upper fire is withdrawn, and the contents of the upper vessel are run off into the lower, when a copious precipitate is formed, consisting of mono-hydrated carbonate of soda. The whole is kept boiling, and the precipitated salt is ladled out into a draining vessel, placed so, that the liquid which runs off may be returned to the boiler.

The solution in the lower vessel is then somewhat concentrated by evaporation, and the carbonate of soda which crystallizes out is removed as completely as possible,—an operation much facilitated by the acicular and granular form of the salt; the boiler is then filled up with pure water, and the diluted solution is boiled and left to settle, and drawn off, after a few hours, into the crystallizing vessels. Pure saltpetre is then deposited in large crystals, or, if the liquid is agitated, as a crystalline powder.

By washing this powder with water, the saltpetre is obtained very nearly pure. The mother-liquor is used to dissolve the nitre and potash in a subsequent operation.

To obtain the saltpetre which remains attached to the precipitated carbonate of soda, the lower boiler—or any boiler heated in a similar manner—is half filled with water, and the precipitated soda, is thrown in till it is full. The liquid is now heated to the boiling point, so as to saturate the water with the salt; the undissolved residue is taken out and left to drain as before; fresh soda-salt is thrown in; and these operations are repeated till the solution no longer takes up any more carbonate of soda, but only saltpetre. When, by this means, the solution is sufficiently charged with saltpetre, it is evaporated till it deposits carbonate of soda, and is treated just like a fresh solution of nitrate of soda and carbonate of potash.

By this process, 100 parts nitrate of soda yield 100 parts or more of nitrate of potash. The soda-salt may be sold as such or recrystallized. The amount of nitrate of potash obtained ought to be greater, but the nitrate of soda is never pure.

An addition of glue to the solution of saltpetre before it is left to clarify is advantageous, as the gelatin surrounds the suspended particles of carbonate of lime, &c., and forms them into lumps, which settle down more quickly.

Another arrangement is described by Wölner* in Cologne. A number of large iron vessels, 5 feet in diameter and 4 feet deep, containing a solution of carbonate of potash (*Potaschenlange*) of 42° Bm. (sp. gr. 1·4), are placed over a somewhat enclosed trough set in cement, through which the lye, after it has become clear, may be run off into a reservoir provided with a pump. In a lower apartment is placed a large tub, in such a manner that a second tub having a double bottom may rest upon the edge of the first and project 3 feet above the floor of the factory. About 5 tons of Chili saltpetre are introduced into the upper tub, and a stream of water is made to play upon it, fresh nitre being continually added as the mass in the upper vessel sinks. The solution of the salt may be continued in this manner for a fortnight or three weeks before the tub requires cleansing, a solution of nitrate of soda of 42° B. continually running into the lower tub, whence it may be pumped up when wanted.

The proportions of salt in the two solutions having been ascertained, they are pumped up into large smooth-bottomed pans of iron plate, 15 feet long and 6 feet broad, care being taken that the two salts are mixed in equivalent proportions. The mixed lye is now concentrated to a density of 48 to 32° Bm., the carbonate of soda, which separates all the while, being scraped to one side of the pan and then left in the hot liquid till a sufficient quantity has accumulated to fill the filtering box.

This box, which is the chief peculiarity of the apparatus, consists of a cylindrical vessel of iron plate, 2 feet in diameter and 2½ feet deep, having a perforated false bottom, below which is an iron cock. It has a rim 3 inches broad, to which an iron lid fits, and between the rim and lid is placed a thick bundle of linen cloth, rammed in with iron wedges, so as to make the whole vapour-tight; a vapour-cock is placed just below the rim. This filtering apparatus serves to separate the soda completely from the nitrate of potash by their different specific gravities. A concentrated solution of carbonate of soda at 100° C., has a specific gravity of 1·31—1·32 or 35° Bm., while a boiling hot concentrated saltpetre-lye has a density of 50—48° Bm. If now steam be admitted into the apparatus through the cock below the rim, as much of it will be condensed as the soda-lye is able to take up, the lye being thereby reduced in specific gravity. On opening the lower cock, the concentrated saltpetre-lye, which occupies

* Polytechnisches Notizblatt, 1860, p. 49; Wagner's Jahresbericht der Chemischen Technologie, 1860, p. 204.

the lowest place, runs off first, the filtrate becoming more and more alkaline as the saltpetre-lye is displaced by the carbonate of soda, and ultimately when the lye which runs off exhibits a density of 35° Bm., the soda-solution no longer retains any saltpetre. In this way alone is it possible to obtain 110 parts of nitrate of potash (the calculated quantity) from 100 parts of Chili saltpetre (containing 95 parts nitrate of soda).

The filtering apparatus just described stands upon two iron supports laid over the hinder end of the pan, so that the saltpetre-solution which runs off mixed with soda-lye may flow back into the pan. The evaporation is continued, and the soda removed once or twice more in the same manner. The saltpetre-lye is then transferred to iron pans to crystallize. The Chili saltpetre-lye in the lower tub must be measured by a proper graduation, and the measures duly observed in pumping it out: similarly with the potash-lye. In this manner the right proportion of the two liquids may be determined once for all, inasmuch as the strength of each solution is known. If in the course of the process, an excess of either solution is found to be present, the requisite quantity of that which is deficient must be added.

The amount of saltpetre in the soda may be estimated by the following method depending on the decomposibility of indigo by nitric acid. A solution of pure indigo—best of indigo-blue—in sulphuric acid is diluted with a large quantity of water, and a standard solution is prepared, 10 parts of which correspond to 1 part of nitre. 100 parts (about 6 grm.) of the soda which is to be tested for saltpetre are then weighed out, sulphuric acid free from nitric acid is added, and the whole boiled. The standard solution is now added till the blue colour changes to scarlet and orange, and the quantity of liquid used for the purpose is read off. This method will serve for the correct estimation of $\frac{1}{100}$ part of saltpetre.

In Belgium, large quantities of saltpetre are prepared by decomposing nitrate of soda with potash obtained from the ashes of the beet-root sugar-works. The saltpetre obtained by this process is very pure, not containing more than from 0·0055 to 0·0060 per cent of chlorine, and a mere trace of sulphates. It is also produced at a very low price.

Preparation of Nitrate of Potash from Nitrate of Soda and Chloride of Potassium.

When solutions of nitrate of soda and chloride of potassium are mixed in equivalent proportions (74·7 parts KCl to 85 parts $NaNO^6$), double decomposition takes place, and on evaporation, chloride of sodium crystallizes out, while nitrate of potash remains in the hot mother-liquor and crystallizes on cooling. The process was first introduced by Mr. F. C. Hills.* The following details are given by Anthon.†

The first thing to be done is to ascertain the proportions of pure nitrate of soda and chloride of potassium in the materials used.

Commercial nitre seldom contains more than 90 per cent. of pure nitrate of soda. The valuation may be performed as follows, with sufficient accuracy for manufacturing purposes.

100 grains of the sample are spread out on a watch-glass and exposed to a moderate heat as long as its weight decreases. The loss gives the water. About 1½ to 3 oz. are then to be covered with an equal quantity of water and agitated without heating, till a concentrated solution is formed, and the temperature has fallen to that of the surrounding air. The solution is then to be decanted, filtered if necessary, and its specific gravity ascertained. If it amounts to 1·377 at 15° R. (65·75° F.), the Chili saltpetre may be considered sufficiently pure: if lower, it contains common salt. With 1 per cent. common salt, the specific gravity is 1·375; with 5 per cent. it is 1·369; with 32 per cent. it is 1·359. Any larger amount of common salt has no further influence on the density; but it never occurs.

This method depends upon the fact, that nitrate of soda, *per se*, is much more soluble than in presence of chloride of sodium; 100 parts of water at 15° R. dissolve 88 parts of pure nitrate of soda, but only 52·82 parts together with 24·98 chloride of sodium (= 77·8), if water be saturated with the two salts together. A solution of nitrate of soda saturated at 15° R. has a specific gravity of 1·377; at 10° R. = 1·366. At 18¾° R. nitrate of soda dissolves in 1·136 parts of water.

Chloride of Potassium is chiefly manufactured in Scotland from kelp, and its value is guaranteed at 80 per cent. It is also

* Date of patent, 1846, No. 11,326.

† Dingler's Polytechnisches Journal, cxlix. 40.

obtained as a by-product in the preparation of red prussiate of potash; this product is purer than the Scotch, but is not always to be obtained in sufficient quantity. Lastly, it is contained in the waste products of the saltpetre refinery, which, however, do not contain more than 50 per cent. KCl, and moreover NaCl.

To estimate the degree of purity of this salt, a glass cylinder $\frac{1}{2}$ to $\frac{3}{4}$ inch wide, is graduated from the bottom upwards, in such a manner, that each degree shall be equal to the space which is occupied by the quantity of alum-flour recently precipitated by 1 grain of potash in the equivalent quantity of chloride of potassium, from a solution of sulphate of alumina saturated with potash-alum,—after it has acquired its greatest density by frequent agitation of the cylinder. A degree thus determined, is equal to the space occupied by 8·6 grains of water at 12° R. (59° F.)

To use this measure, 100 grammes of the chloride of potassium under examination, are dissolved, with aid of heat, in a solution of sulphate of alumina previously saturated with potash-alum at the temperature of the air, and containing a quantity of alumina sufficient to convert into alum the whole of the potash contained in the chloride of potassium, if this salt were quite pure. If, for example, the sulphate of alumina has been dissolved in its own bulk of water, about 1000 grains of the solution will be sufficient to dissolve 100 grains of chloride of potassium. It will of course be understood, that the original volume of the sulphate of alumina solution must be restored by the addition of water, if any portion of it has been volatilised by the heat.

The chloride of potassium having been dissolved in the sulphate of alumina solution, the liquid while still warm, is introduced into the measuring glass, the vessel tightly closed, and then shaken with frequent immersion in cold water, until no further deposition of alum takes place and the solution has fallen to the temperature of the surrounding air. The cylinder is then cautiously tapped on a wooden stand, till the deposit has assumed its normal volume, after which the percentage of chloride of potassium in the sample may be read off on the scale.

The following are examples of the results obtained by this method.

Samples of commercial chloride of potassium.	Volume of alum flour precipitated.	Percentage of pure KCl.
Perfectly pure	63	100·0
From the preparation of red prussiate .	61	97·0

Samples of commercial chloride of potassium.	Volume of alum flour precipitated.	Percentage of pure KCl.
Scotch	48	76·2
„ another sample	57	90·5
„ a third sample	52	82·5
From a saltpetre refinery	41	65·0
„ „	36	57·1
„ „	32	50·8

Chloride of potassium dissolves in 3 times its bulk of water at 17·5 R. forming a liquid of sp. gr. 1·163. According to Gay-Lussac 100 parts water at 0° C. dissolve 29·23 parts chloride of potassium, and 0·2738 parts more for every degree above 0°.

The process of manufacture is as follows:

A quantity of water equal to or rather greater, than the quantity of nitrate of soda to be converted, is first heated in an iron boiler or other suitable vessel; the nitrate of soda is then added, with constant stirring; and when it is completely dissolved, and the temperature of the liquid has risen to the boiling point, the equivalent quantity of chloride of potassium is added, and the liquid kept in a state of ebullition for half-an-hour. The salts do not dissolve to a clear liquid, because the quantity of water present is not sufficient to retain in solution the whole of the chloride of sodium formed: this salt, therefore, swims about in the liquid as a crystalline powder, and may be removed by means of a number of small basins suspended in the liquid. When these basins have become filled with chloride of sodium, they are taken out and emptied; the bottom of the boiler is scraped with an iron rod sharpened and hardened at the end, to detach the chloride of sodium which has settled upon it; and the basins are again immersed in the liquid.

The hot chloride of sodium thus removed, is left to drain in casks, the bottoms of which are covered with straw or twigs, upon which a very coarse cloth is laid; the vessels are also pierced with holes at bottom, and are so placed, that the mother-liquor which drains from the salt, may run back into the boiler. As soon as one of these vessels is full of salt, water or a solution of chloride of sodium is poured in at the top, as long as the liquid which runs out appears warm and exhibits a density of 25° B. When this is no longer the case, it is a proof that all the saltpetre has been washed out.

The boiling and the other operations just described, are continued till the liquid in the boiler has attained a density of 40—42° B. (while hot). The boiler is then covered, and the liquid is left at rest, till it has become clear, then drawn off hot by means of a leaden siphon into the crystallizing vessels.

The crystallization and purification of the saltpetre thus obtained, are conducted much in the same manner as in the processes already described. The crude saltpetre obtained by the first crystallization contains, after draining, about 1 per cent. of chloride of sodium. By grinding the crystals, saturating the crystalline powder with water, leaving it to stand for 18—24 hours, and then draining off the liquid, the amount of chloride of sodium is reduced to $\frac{1}{3}$ per cent. The saltpetre thus purified, is then redissolved and recrystallized, the mother-liquor being used for washing the crude saltpetre in subsequent operations. The wash-waters and mother-liquors of the crude saltpetre are used for the first boiling of fresh quantities of material.

As the degree of purity of the raw materials used cannot always be tested, an excess of either nitrate of soda or chloride of potassium will sometimes be present in the mother-liquors, and will attach itself to the crystals of crude saltpetre. These salts are easily recognized by their crystalline forms, the nitrate of soda forming rhombohedrons, and the chloride of potassium cubes. According as one or the other salt is formed in excess, the deficient ingredient may be added to the liquid during the boiling.

The mother-liquor which remains after the first crystallization, is a saturated solution of nitrate of potash and chloride of sodium; and, if neither of the original salts is present in excess, it has a specific gravity of 1·325 = 35½° B. The addition of chloride of potassium does not increase its density, because a proportional quantity of chloride of sodium separates. If, on the other hand, nitrate of soda be added to it, the density increases, because this salt, in dissolving, does not separate quite an equivalent quantity of nitrate of potash or chloride of sodium from the liquid. The addition of a quantity of nitrate of soda equal to about $\frac{1}{10}$ of the weight of the liquid, increases the density to 1·345. Hence, if the density of the mother-liquor exceeds 1·325, the cause of the increase will generally be found to be due to the presence of an excess of nitrate of soda.

The advantages of the process are as follows:

1. The decomposition of nitrate of soda by chloride of potassium is rapid and complete.

2. The cleansing of the deposited chloride of sodium from adhering nitrate of potash is also rapid and complete.

3. The purification of the saltpetre from adhering common salt is also easy and perfect.

4. If the process is performed without loss, the yield is very considerable, 100 parts of nitrate of soda yielding 118 parts of nitrate of potash.

5. The ordinary impurity of the two raw materials used, does not interfere with the process, inasmuch as the same substance, viz., chloride of sodium, is a product of the decomposition.

6. The process may be carried on with great regularity, and the working up of the mother-liquors is easily managed.

Use of Baryta-salts in the preparation of Saltpetre from Nitrate of Soda.—It has been proposed to manufacture saltpetre from nitrate of soda, by first converting the latter salt into nitrate of baryta by means of chloride of barium, and then decomposing the nitrate of baryta with sulphate or carbonate of potash. When 1 eq. chloride of barium (122 parts $BaCl.2HO$) dissolved in twice its weight of water, is mixed with 1 eq. nitrate of soda (85 parts $NaNO^6$) dissolved in an equal weight of water, and the solutions are mixed hot, nitrate of baryta is formed and separates out, for the most part, as the liquid cools, a certain proportion however always remaining in solution, varying according to the purity and dryness of the materials used, but never exceeding 14 per cent. of the whole.

The nitrate of baryta thus obtained, is decomposed by an equivalent quantity of sulphate or carbonate of potash. In either case, the whole of the baryta is precipitated as sulphate or carbonate, while nitrate of potash remains in solution, and may be obtained pure by filtration and crystallization. When sulphate of potash is used, a precipitate of sulphate of baryta is obtained, which, when washed and dried, may be sold as a pigment; and when the precipitation is performed with carbonate of potash, carbonate of baryta is obtained, which may be converted into chloride of barium by hydrochloric acid, and used again.

The baryta which remains in solution, after the separation of the nitrate in the first stage of the process as above described,

may likewise be recovered by precipitation, either as sulphate or as carbonate. (Bolley, *Wagner's Jahresbericht*, 1860, p. 202.)

Samuel Cooper, of Boston (U. S.), has patented a process* by which he obtains nitrate of potash, together with carbonate of lead and sulphate of soda. The process consists in first dissolving lead in nitric or acetic acid, decomposing the resulting solution with sulphuric acid, so as to form sulphate of lead, and treating this sulphate with carbonate of potash and nitrate of soda.

The lead should be finely divided, so as to facilitate its solution. The following method has been found to answer the purpose:—Melt metallic lead, and pour it through a perforated vessel into water; the lead is thus reduced to a finely-divided state, and in this state it is placed in a vessel of wood or other suitable material; the vessel is then charged with a sufficient quantity of diluted nitric acid to cover the lead, which is immediately attacked. After standing for some time, the acid is drawn off upon a quantity of similarly prepared lead in a second vessel, where it is allowed to remain, as before, in contact with the lead for a short time; it is then again drawn off upon a third quantity of lead in another vessel, and here it is allowed again to stand. The neutral nitrate of lead is now treated with sulphuric acid, which is gradually added until the nitrate is all decomposed, an insoluble sulphate being formed, which is precipitated, while the nitric acid is again set free. The latter is then drawn off, and is returned to the original tub of the series, to act upon a fresh supply of lead. The nitric acid is thus constantly made available for the continuance of the operation, and may be used over and over again, until lost by wasting, or weakened or deteriorated by foreign substances introduced by the reagents employed.

It is obvious that a greater or smaller number of tubs may be employed in a series, the operation of dissolving the lead being greatly hastened by the successive drawings off and the consequent exposure of the lead to the action of the atmosphere. An excess of lead must be employed, to ensure the saturation of the nitric acid, and sufficient sulphuric acid to effect the entire decomposition of the nitrate of lead, the latter part of the operation being easily tested as it proceeds. In place of nitric acid, acetic acid may be employed for the purpose of dissolving the lead, the resulting acetate being decomposed, as in the case

* Date of patent 27th May, 1859; No. 819.

of the nitrate, by sulphuric acid, which again sets the acetic acid free for future use.

The above process may be modified as follows:—A saturated solution of nitrate of soda in water is decomposed by 30 to 40 lbs. of sulphuric acid of 66 per cent., which is generally sufficient to decompose 100 lbs. of the nitrate of soda of commerce. Nitric acid is thus set free, and sulphate of soda is formed. The whole is then heated to 200° Fah. in pots of stoneware or enamelled iron, and metallic lead is introduced, which will be rapidly dissolved by the nitric acid, the nitrate of lead thus formed being forthwith decomposed by the sulphate of soda, yielding an insoluble precipitate of sulphate of lead and a solution of nitrate of soda. As the sulphuric acid is expended, it is replenished from time to time; and when the lead is all dissolved, the solution of nitrate of soda is decanted upon a new portion of lead, to be treated with a fresh supply of acid, thus using continuously the same solution of nitrate of soda with renewed portions of sulphuric acid and lead as before.

Secondly, the sulphate of lead thus obtained is decomposed by means of carbonate of potash and nitrate of soda. For this purpose, 25 lbs. of sulphate of lead are added to a saturated solution of 10 lbs. of pearlash in water. A double decomposition then takes place, resulting in the formation of sulphate of potash and carbonate of lead; the latter, being an insoluble precipitate, may be separated from the solution of sulphate of potash by decantation. The sulphate of potash is now decomposed by the addition of nitrate of soda, 12½ lbs. of the latter being added for the above quantities of sulphate of lead and pearlash, or in that proportion, saltpetre and sulphate of soda being the result; the two salts are then separated by crystallization. The materials employed are thus all converted into marketable products, viz., carbonate of lead (the white lead of commerce), nitrate of potash (saltpetre), and sulphate of soda (Glauber salts).

Or again:—The nitrate of soda is boiled with the pearlash, the result being nitrate of potash and carbonate of soda, and the former is separated by crystallization. The carbonate of soda is then employed to decompose the sulphate of lead, and the resulting compounds are carbonate of lead, nitrate of potash, and sulphate of soda; or the nitrate of soda, the sulphate of lead, and the pearlash may be mixed together at once, and will yield the three products above mentioned.

TESTING FOR PURITY, OR REFRACTION OF SALTPETRE.

In most countries, those persons who are commissioned to purify saltpetre for the use of the army, obtain the crude saltpetre from the regular manufacturers. As a considerable portion of the weight of this product is always due to foreign matters, and its value is solely dependant on the amount of pure saltpetre which it contains, it becomes important to have some means of ascertaining its value with sufficient accuracy and in a speedy manner, so that the course of business may not be suspended by the investigation. The object of testing the crude material is, therefore, to ascertain the amount of pure nitrate of potash which it contains: it is also sometimes advisable to know how much nitrate of soda may be present, as that salt adds to the value of crude saltpetre. The methods which are generally employed afford no scientific accuracy, nor is that absolutely necessary for practical purposes.

Swedish process.—In Sweden, where saltpetre is levied as a duty upon every landed proprietor, the samples for testing accumulate to such an extent, that the easiest, though not the most accurate, plan has been necessarily adopted. The method was introduced by G. Schwartz, and consists in casting the melted salt in the form of a cake, 1 inch in thickness, in a small tin box, and examining its fracture in the manner already explained. This casting is, of course, only necessary when the crude saltpetre is not delivered in this form by the producer, and he is not legally obliged to return it in that state. That which shows a radiating fracture, or is found to present it on fusion, must be accepted; that which does not, is valued by the collector, who is at liberty to take a larger quantity as compensation for the inferior quality.

Riffault's process.—In France, saltpetre is tested in the humid way by a process introduced by Riffault. A weighed quantity of the dry crude saltpetre is gradually washed, at the temperature of the testing-room, with a saturated aqueous solution of pure saltpetre. When as much of this solution has been used for washing, as would be sufficient to dissolve four or five times as much chloride as can possibly be contained in the worst sample of crude saltpetre, it is then quite certain that nothing but pure saltpetre can remain. For a sample weighing $12\frac{2}{5}$ oz., $18\frac{1}{2}$ oz. of a pure solution of

saltpetre are used, which will dissolve 8½ oz. of common salt, or 66 per cent. of the sample, a quantity which is never actually present. Nothing now remains to be done but to weigh the saltpetre remaining upon the filter; there is, however, some difficulty attending this, as the solution which adheres to it must first be removed. To effect this, the filter is spread out upon blotting paper, placed upon a porous substance (a slab of gypsum, for instance), and, at the expiration of twenty-four hours, the saltpetre is taken out and dried. From the weight found, which indicates the amount of saltpetre in the sample, 2 per cent. must always be deducted, as that quantity has been found by experiment to remain in the wash-water, and cannot be completely removed.

Gay-Lussac's method.—It is obvious that the process just described must be both tedious and inaccurate; Gay-Lussac, therefore, proposed the use of his alkalimeter as a means of testing saltpetre. With this view, the saltpetre must be converted into carbonate of potash by fusion with charcoal, when all the nitrogen is evolved. That the evolution of gas may not be too violent, and a portion of the test be lost, 8 parts of common salt, which do not affect the test, are mixed with 1 part of charcoal powder or soot, by way of dilution, and the whole is brought into a state of fusion in an iron spoon. The fused saline mass gives a solution of carbonate of potash and chloride of sodium, which must be filtered, and treated with the test-acid in the manner described under ALKALIMETRY. Every atom per cent. of potash indicated by the alkalimeter, proves the presence of 2·14 per cent. of saltpetre; every atom per cent. of carbonate of potash, 1·46 of saltpetre in the sample tested.

This method has lately been submitted to a minute examination by Messrs. Abel and Bloxam,* who find that it does not always give exact results, partly because a portion of the nitre often escapes decomposition, and partly because cyanate of potash is formed during the reaction, and, when subsequently dissolved in water, is decomposed, forming carbonate of potash and carbonate of ammonia:

$$C^2NO.KO + 4HO = KO.CO^2 + NH^4O.CO^2,$$

thus making the quantity of alkali to be neutralized, greater than it should be. The presence of alkaline sulphates in the nitre also introduces an error, because these salts are reduced by ignition

* Quarterly Journal of the Chemical Society, ix. 97; x. 107.

with charcoal to sulphides, which have an alkaline reaction. Messrs. Abel and Bloxam find, however, that these sources of error may be eliminated and exact results obtained, by using the charcoal in a very finely divided state, and finally heating the ignited mass with chlorate of potash, which completely decomposes the cyanates and reconverts the sulphides into sulphates. The best form of carbon for the purpose, was found to be the pure finely-divided graphite prepared by Brodie's process, which consists in mixing coarsely-pounded graphite with $\frac{1}{10}$th of its weight of chlorate of potash, adding the mixture to a quantity of strong sulphuric acid equal to twice the weight of the graphite, heating the mixture in the water-bath as long as vapours of peroxide of chlorine are given off, washing the cooled mass with water, and igniting the dry residue: it then swells up and leaves finely-divided graphite.

Husz's method.—A method very different from either of the two preceding, is that proposed by Husz, colonel of artillery, and introduced by him into Austria. His method is a physical analysis, and is founded upon the fact, that the temperature at which a cooling solution of saltpetre loses the property of dissolving more saltpetre, or, what is the same thing, the temperature at which it begins to deposit crystals (in fact, its point of saturation) is a fixed temperature, and depends solely upon the relative proportion of water to that of the saltpetre dissolved, whether chlorides are present or not.

If, therefore, the quantity of water remains the same in different cases, the point of saturation will solely depend upon the quantity of saltpetre; and the temperature at which saturation occurs will be a means of ascertaining the amount of saltpetre in a given specimen. Experiments must have been previously made to determine the point of saturation of solutions containing different quantities of saltpetre in an equal amount of water. Such experiments have been made in sufficient number, and arranged in a tabular form, showing, for all the points of saturation, and for every quarter of a degree R., the quantity of saltpetre contained in 100 parts of water, or the percentage of the solution.

Temperature. Réaumur.	Quantity of pure saltpetre in 100 parts of the solution.	Quantity of pure saltpetre in 100 parts of the sample.	Temperature. Réaumur.	Quantity of pure saltpetre in 100 parts of the solution.	Quantity of pure saltpetre in 100 parts of the sample.
+8°	22·27	55·7	+14·25°	30·00	75
8·25	22·53	56·3	14·50	30·36	75·9
8·50	22·80	57·0	14·75	30·72	76·8
8·75	23·08	57·7	15	31·09	77·7
9	23·36	58·4	15·25	31·46	78·6
9·25	23·64	59·1	15·50	31·83	79·6
9·50	23·92	59·8	15·75	32·21	80·5
9·75	24·21	60·5	16	32·59	81·5
10	24·51	61·3	16·25	33·97	82·4
10·25	24·81	62	16·50	33·36	83·4
10·50	25·12	62·8	16·75	33·75	84·4
10·75	25·41	63·5	17	34·15	85·4
11	25·71	64·3	17·25	34·55	86·4
11·25	26·02	65	17·50	34·90	87·4
11·50	26·32	65·8	17·75	35·38	88·4
11·75	26·64	66·6	18	35·81	89·5
12	26·96	67·4	18·25	36·25	90·6
12·25	27·28	68·2	18·50	36·70	91·7
12·50	27·61	69	18·75	37·15	92·9
12·75	27·94	69·8	19	37·61	94
13	28·27	70·7	19·25	38·01	95·2
13·25	28·61	71·5	19·50	38·55	96·4
13·50	28·95	72·4	19·75	39·03	97·6
13·75	29·30	73·2	20	39·51	98·8
14	29·65	74·1	20·25	40	100

In order, therefore, to ascertain the value of a specimen of crude saltpetre, a weighed quantity must be dissolved in 100 parts of water at about 48° R. (140° F.), and the sinking of the temperature must be watched with a thermometer indicating one-fourth of a degree, until crystals begin to deposit. The point of saturation is then attained (or, in reality, is a little exceeded), and the temperature observed at the moment, compared with the table, will indicate the quantity of saltpetre contained in the solution.

The quantity indicated by the table, calculated for the actual quantity employed, gives the real value of the specimen. Suppose the test to have been made with 40 parts of crude saltpetre, and the point of saturation to have been attained at 14·25 R.: this solution would contain, according to the table, 30 parts of saltpetre; these 30 parts were obtained from the weighed specimen, which consequently contains ¾ths = 75 per cent. of pure saltpetre. The specimen must be thoroughly dry when used, or more water would be present than is estimated in the

results given in the table. The mutual decomposition of chloride of sodium and saltpetre, which, by the production of nitrate of soda, causes an apparent greater solubility of saltpetre in water containing chloride of sodium, may give rise to a slight inaccuracy in this method, which, in rapidity of execution, comes next to the Swedish.

According to F. Toel* Husz's method gives exact results only when 40 parts of the saltpetre to be tested are dissolved in exactly 100 parts of water at 45° R. (133½ F.), the solution subsequently cooled by immersing the vessel in cold water, and the temperature at which crystallization begins, carefully observed, the solution being constantly stirred as it cools. To ensure the right proportion, the saltpetre is dissolved in the proper quantity of water contained in a tared beaker glass with a thermometer inserted, and heated to 45° — 50° R. in a water bath, the water which evaporates while the salt is dissolving, being replaced. The solution is filtered, to remove any solid particles suspended in it, which might cause the crystallization to take place too soon; and the first half which runs through is used for observing the temperature at which crystallization begins. With 10 drachms of saltpetre and 25 drachms of water, the quantity of water which evaporates during the operation generally amounts to 8 or 10 grains, and that which is lost during the cooling and stirring, to 2 or 3 grains.

By this method, Toel and Hoyermann also determine the amount of nitrate of soda in nitrate of potash, an impurity which generally exists in the nitre prepared from Chili saltpetre, in consequence of imperfect decomposition. The amount of nitrate of potash is first determined, in the given sample, exactly in the manner just described; then about 7½ drachms are dissolved in 25 drachms of water; a drachm of carbonate of potash is added; the crystallizing point is observed; and the solution then boiled for an hour, to convert the nitrate of soda completely into nitrate of potash. The solution is now left to cool to 50° R., the water being replaced as it evaporates, then filtered, and the crystallizing point again observed. If the sample contained nitrate of soda, the crystallizing temperature will now be found higher than before, viz., 0·15° R. for 1 per cent. of nitrate of soda, 0·35° R. for 2 per cent., 0·8° R. for 3 per cent., and 1·55° R. for 4 per cent.

The amount of nitrate of soda in saltpetre may also be approxi-

* Ann. Ch. Pharm. c. 78.

mately determined by ascertaining the quantity of water which it absorbs when exposed to an atmosphere saturated with moisture.

According to the observations made by the Prussian officers of artillery, it appears that pure nitrate of potash exposed over the surface of water for fourteen days, remains comparatively dry, whilst nitrate of soda placed under the same circumstances, absorbs 25 per cent. of water. When artificial mixtures of the two salts in a pure state are subjected to the same treatment, the quantities of water absorbed, are as follows:

Mixture with percentage of nitrate of soda.	0·5	1	3	5	10	
Absorbed in 14 days	2·5	4	10	12	19	Water, per cent.

All gunpowder containing this variety of saltpetre would, of course, become moist in the same proportions, and would thus be rendered useless; hence, the necessity for ascertaining the absence of nitrate of soda in saltpetre for all purposes connected with gunnery.

A third method of determination is based upon the alteration which an admixture of nitrate of soda produces in the solidifying point of saltpetre heated above its melting point. Nitrate of potash melts at 358° C. (674·4° F.), and nitrate of soda at 313° C. (595·4° F.). For mixtures of 100 parts nitrate of potash with different proportions of nitrate of soda, the following melting points have been observed.

Quantities of $NaO.NO^5$ added to 100 parts $KO.NO^5$.	Melting points.
10 parts	311° C. = 591·8° F.
20 „	280° = 586·0°
30 „	250° = 482·0°
40 „	230° = 446·0°
45·7 „	226° = 438·8°
50 „	229° = 444·2°
60 „	244° = 471·2°
70 „	262° = 503·6°
80 „	281° = 537·8°
90 „	298° = 568·4°

The lowest melting point is exhibited by a mixture of the two salts in equivalent proportions (45·7 per cent. of nitrate of soda), which, according to Schaffgotsch, melts at 226° C., and according to Persoz, at 219·8° C.

For detecting the presence of a small quantity of nitrate of soda in nitrate of potash, advantage may be taken of the yellow colour which soda-compounds impart to the blowpipe flame. According to H. and P. Reinsch* a quantity of soda not exceeding 0·5 per cent. may be detected in nitre, by placing about 5 grains of the sample in a small cavity on a piece of well-ignited charcoal, and directing the blowpipe flame on the edge of the cavity till the nitre deflagrates.

Much smaller quantities of soda mixed with potash, may be detected by the method of Bunsen and Kirchhoff,† which consists in observing the bright lines in the spectrum of a faintly-coloured flame, like that of a Bunsen's gas-burner, in which a small quantity of the substance to be tested, is ignited. Soda-compounds thus treated, produced a spectrum reduced to a single bright yellow line, coinciding in position with the dark line D of the ordinary solar spectrum. This line is quite as conspicuous in presence of potash as without it, and is distinctly visible when the quantity of soda present is reduced to a mere trace, which cannot be recognized by any of the ordinary methods of chemical analysis.

The only test for the chloride (the usual impurity) in purified saltpetre, is nitrate of silver, which produces a precipitate of chloride of silver, corresponding to the quantity of chloride present.

Gossart and Pelouze's method.—The ease with which nitric acid converts a proto-salt of iron into a per-salt of the metal, has been made available by M. Gossart as a means of testing the relative purity of crude saltpetre. The nitrate under examination is heated with sulphuric acid to liberate the nitric acid, and this is caused to act upon protosulphate of iron : when ferrocyanide of potassium indicates the presence of an excess of proto-salt, the operation is finished, and the amount of nitric acid in the nitrate is estimated by the quantity of the proto-salt which has been peroxidized.

There is some practical difficulty experienced in adding the exact quantity of proto-salt of iron required in this process, and if any excess of proto-salt has been used, it will of course give rise to

* Jahrbuch pr. Pharm. vii, 19.

† Pogg. Ann. cx, 1 ; Quart. J. of Chem. Soc. xiii, 270.

an error indicating too much nitric acid in the substance analysed. Pelouze obviates this difficulty by employing a known excess of the proto-salt of iron in the preceding process, and then estimating the quantity of iron not peroxidized by the nitrate, in the manner proposed by Marguerite for analysing iron ores. Marguerite has shown that a dilute solution of protochloride of iron is instantly peroxidized when a solution of permanganate of potash is added to it at the ordinary temperature, and that the addition of the smallest quantity of mineral chameleon to a salt of iron thus peroxidized, communicates a rosy tint to the liquid, which indicates distinctly the completion of the peroxidation.

Having previously ascertained that 2 grammes of pure iron, dissolved in a considerable excess of hydrochloric acid, require, on an average, 1·216 grms. of pure nitrate of potash to peroxidize them, the process is then conducted as follows: 2 grms. of harp wire are placed in a flask capable of holding 150 cubic centimetres, and from 80 to 100 grms. of pure strong hydrochloric acid are poured upon it; the flask is then closed with a cork furnished with a tube drawn out to a point, and the iron is dissolved at a gentle heat. When the whole is dissolved, 1·200 grms. of the nitre under examination is introduced, the flask is immediately closed, and the liquid boiled; it soon becomes of a brown colour; and dense vapours of hydrochloric acid, mixed with binoxide of nitrogen, issue from the orifice of the tube, preventing the access of air. The liquid soon loses its brown colour, becomes yellow and clear, and after it has boiled for 5 or 6 minutes, and become perfectly transparent, the flask containing it is removed from the fire, and the liquid is poured into another flask capable of holding about 1 litre, which is then completely filled with distilled water; into this, a solution of permanganate of potash of known strength is cautiously added from a graduated jar. The flask is agitated, in order to mix the liquid, and as soon as the solution assumes a faint rosy tint, the addition of permanganate is discontinued, and the quantity employed to peroxidize the iron is read off on the jar.

Now, supposing that the strength of the solution of permanganate were such as would require 50 cubic centimetres for the peroxidation of 1·0 grm. of iron, and that 10 cubic centimetres had been employed in the example above; we should then have the equation:

$$50 \text{ c. c.} : 1{\cdot}000 :: 10 \text{ c. c.} : x = 0{\cdot}200.$$

On deducting, therefore, 0·200 from the whole amount of iron

used, we obtain the quantity of iron peroxidized by the agency of the nitrate, or 2·000 — 0·200 = 1·800; but as 2 grms. of iron correspond to 1·216 of pure nitrate, and 1 grm. consequently to 0·608, the quantity of salt corresponding to 1·800 of iron, will be found by the following calculation:

$$1{\cdot}000 : 0{\cdot}608 = 1{\cdot}800 : x = 1{\cdot}0944.$$

In the 1·200 of crude nitre submitted to analysis there was, consequently, 1·0944 pure nitrate of potash, or $\frac{1{\cdot}0944}{1{\cdot}2000} = 91{\cdot}2$ per cent.

Access of air to the flask, during the operation, should be avoided, as the nitric oxide which is generated would, by its means, become converted into a higher oxide, and thus peroxidize a further portion of the salt of iron. The proto-salt of iron dissolved in an excess of hydrochloric acid, is oxidized with great difficulty on exposure to the air, and no error need be apprehended on that account.

The base, of course, is not indicated by this process, but it is peculiarly adapted for analysing mixtures of sulphuric and nitric acids, used in the manufacture of gun-cotton, for mixtures of nitric acid with water, and more particularly for saltpetre. The process scarcely requires twenty minutes for completion, and is said by Pelouze to be accurate within two or three thousandths. According to Abel and Bloxam, however,* the results obtained by it are not always exact, because it sometimes happens that a portion of the nitre does not contribute to the oxidizing action, either from not being completely decomposed, or from losing a portion of its acid before it comes in contact with the iron-salt.

According to Fresenius† these sources of error may be obviated and exact results obtained by conducting the process as follows:— A long-necked tubulated retort, having a capacity of about 200 cubic centimetres, being placed with its neck inclined slightly upwards, about 1·5 grammes of pure iron wire is introduced into the bulb, and from 30 to 40 cubic centimetres of pure fuming hydrochloric acid is poured in. A stream of hydrogen gas, previously washed with potash-lye, is then passed into the retort, by a glass tube passing through the tubulure, and entering the retort to the depth of about half-an-inch, and the neck of the retort is connected with a U-tube containing a small quantity of water. The bulb of the

* Chem. Soc. Qu. J. ix, 97.

† Ann. Ch. Pharm., cvi, 217.

retort is sunk in a water-bath, and heated gently till the iron is completely dissolved. The solution is left to cool in the current of hydrogen; the current is then strengthened, and a quantity of the saltpetre to be tested (not exceeding 0·4 gramme), having been weighed out in a small test-tube, is introduced, together with the tube, through the neck of the retort into the bulb. The connection of the neck of the retort with the U-tube is then restored; the contents are heated in the water-bath for a quarter of an hour; the retort is then removed from the water-bath, and heated over a lamp to brisk ebullition, till the solution, which is at first dark-coloured from absorption of nitric oxide gas, has acquired the light brown colour of sesquichloride of iron, after which the boiling is continued for a few minutes longer. Care must be taken not to allow any portion of the salt to dry on the sides of the retort. Before the boiling is arrested, the stream of hydrogen must be accelerated, to prevent air from entering through the U-tube as the boiling ceases. The solution, after cooling in the current of hydrogen, is largely diluted with water, and the quantity of iron still remaining as protoxide is determined by means of permanganate or chromate of potash.

By attending to the precautions just described, the following sources of error are eliminated: —1. Re-conversion of a portion of the nitric oxide into nitric acid by oxygen derived from the air remaining in the apparatus. 2. Reduction of a portion of the permanganic acid or chromic acid, by nitric oxide remaining in the liquid. 3. The escape of nitric acid without having acted on the solution of protochloride of iron. This loss is, however, only to be feared when the solution is too dilute.

Another modification of Pelouze's process is that adopted by C. D. Braun,* who boils the saltpetre with a solution of protochloride of iron containing an excess of hydrochloric acid, in an atmosphere of carbonic acid, till all the nitric oxide is driven off, then warms the solution with iodide of potassium, whereby iodine is separated, according to the equation,

$$3Fe^2Cl^3 + K^2 = 6FeCl + 3KCl + I^2,$$

and estimates the liberated iodine by means of hyposulphite of soda.

F. Mohr† recommends dissolving the nitre in a mixture of 20 volumes of oil of vitriol and 80 volumes of water, and cautiously

* Journal für praktische Chemie, lxxxi, 421.

† Lehrbuch der Titrirmethode, 2 Aufl. p. 191.

adding to the solution a graduated solution of protosulphate of iron containing an excess of sulphuric acid, till the brown colour which the liquid assumes no longer disappears on stirring, the temperature of the liquid being maintained between 70° and 80° C. According to Fresenius,* however, this method does not give exact results, partly because the nitric oxide cannot be completely expelled from the liquid without boiling, partly because the termination of the reaction is not indicated with sufficient distinctness.

Reich's method.†—When dry pulverized nitrate of potash or soda is mixed with 4 or 5 times its weight of pounded quartz, and heated to low redness, the whole of the nitric acid is expelled, and its amount may be determined by the loss of weight sustained. The assay is made as follows:—

The nitrate is first melted in a covered platinum crucible at as low a temperature as possible; the loss of weight which it then sustains gives the quantity of moisture present. It is then fused again at the same temperature as before, poured out into a slightly warmed porcelain capsule, pulverized after solidification, and the powder thoroughly dried. Two or three grammes of pulverized quartz are then introduced into a platinum crucible, ignited, and weighed with the crucible when cold. About 0·5 gramme of the fused and dried nitrate is then added, and the whole is well mixed, and weighed again. The covered crucible is then exposed, for half an hour, to a low red heat just visible by daylight, and weighed when cold, together with the cover. The loss of weight gives the quantity of nitric acid. If this equals d, and the weight of the dry nitrate taken is n, then

$$187{\cdot}4\,\frac{d}{n}$$ gives the quantity of nitrate of potash,

$$\text{or } 157{\cdot}4\,\frac{d}{n}$$ „ nitrate of soda.

Sulphates and chlorides are not decomposed at the temperature above-mentioned; at a stronger heat, however, chloride of sodium or potassium may volatilize. The action of reducing gases must also be avoided, on which account a spirit-lamp is better adapted for the purpose than a gas-flame. If the nitrate contains other

* Zeitschrift für analytische Chemie, 1862, p. 41; Wagner's Jahresbericht, 1861, p. 189.

† Journal für praktische Chemie, lxxxiii, 262; Wagner's Jahresbericht, 1861, p. 224.

substances which volatilize at a dull red heat, but not at the temperature of the preliminary fusion, this method is not applicable to it. In general, every loss arising from the volatilization of extraneous substances, will make the amount of nitric acid appear too large. The silicate formed in the reaction sometimes adheres very closely to the sides of the crucible, and cannot be dissolved out by acids; it is, however, easily removed by fusion with carbonate of soda.

*Persoz's method for the complete analysis of Saltpetre.**— The quantity of water is first determined by heating 50 grammes of the saltpetre in a platinum crucible, and weighing it after cooling, care being taken that the heat does not rise much above the melting point. If the saltpetre contains nitrate of lime or magnesia, 1 gramme of dry chromate of potash must be added, to prevent the decomposition of these salts.

To determine the insoluble matters, the fused mass is treated with water, the liquid filtered, and the undissolved matter washed, dried, and weighed. The liquid is then concentrated to a determinate volume, N. The *chlorides* are estimated in this solution by means of two standard silver-solutions, one containing 27 grammes, the other 2·7 grammes of silver in a litre. A cubic centimetre of the former corresponds to 0·01466 grammes of chloride of sodium, or to 0·01864 grammes of chloride of potassium.

The *sulphates* are likewise estimated volumetrically by means of a standard solution of chloride of barium, containing 259·8 grammes of this salt in a litre, and, therefore, corresponding to 0·179 grammes of sulphate of soda or 0·208 grammes of sulphate of potash. To make the determination, 200 cubic centimetres of the solution N, are mixed with a few drops of acid in a platinum dish, then heated to boiling, and the standard solution is cautiously added in slight excess. The saltpetre-solution N is then gradually added from a burette to the liquid contained in the dish, till the excess of the baryta-solution is decomposed and the whole of the baryta precipitated. This last operation is rather tedious, because the liquid does not easily clarify, and it is necessary to filter a sample from time to time. From the proportion between the total volume of the liquid N used in the experiment, and the

* J. Persoz, Rép. Chim. app. 1861, pp. 253, 366; Wagner's Jahresbericht, 1861, p. 225.

volume of baryta-solution present, the amount of sulphate contained in the saltpetre may be calculated.

The nitric acid is estimated by igniting the fused saltpetre with about twice its weight of bichromate of potash, at a moderate heat at first—afterwards, when the evolution of nitrous fumes becomes fainter, to bright redness, with the crucible covered. The loss of weight gives the amount of nitric acid.

Anthon* has endeavoured to estimate the proportion of nitrate of soda in a mixture of that salt with nitrate of potash, by the alteration which it occasions in the specific gravity of a saturated solution, this alteration being considerable even for an amount of only 1, 2, or 3 per cent. of nitrate of soda. But, from the experiments of Piccard and Cornu, made under Bolley's direction,† it appears that the indications afforded by this method are not sufficiently exact, even for technical purposes.

NITRIC ACID.

French, *Acide nitrique* or *azotique*; German, *Salpetersäure*.

This acid has been known for many centuries. It is mentioned in the writings of Geber in the eighth century; Raymond Lullius, in the thirteenth century, gave directions for preparing it by distilling saltpetre with sulphate of iron; and Glauber, soon afterwards, obtained it by distilling saltpetre with oil of vitriol,—the process by which it is prepared at the present day. In 1849, H. Sainte-Claire Deville obtained *anhydrous nitric acid* or *nitric anhydride*, NO^5, in transparent crystals, by decomposing dry nitrate of silver in an atmosphere of chlorine. This anhydrous acid, however, is of interest only in a scientific point of view.

All the nitric acid of commerce contains water: the strongest is that whose composition is expressed by the formula $NO^5.HO$ or NO^6H. This acid contains 85·8 parts by weight of the anhydrous acid, NO^5, and 14·2 parts of water. It has a specific gravity of 1·522, and boils without decomposition at 80° C. (140° F.). It fumes strongly in the air, has an intensely

* Dingl. pol. J. cxlix, 190; Wagner's "Jahresbericht," 1858, p. 152.

† Dingl. pol. J. clxii, 214; Wagner's "Jahresbericht," 1861, p. 222.

pungent odour, and acts with great violence on most vegetable and animal substances. When pure, it is colourless; but by mere exposure to light, it is partly resolved into oxygen, which escapes in bubbles, and peroxide of nitrogen, NO^4, which remains dissolved in the liquid, and gives it a yellow or red colour, according to the extent to which the decomposition has proceeded.

Mono-hydrated nitric acid mixes in all proportions with water, forming acid mixtures decreasing in density as the proportion of water increases. A table of the strength of nitric acid in proportion to its density, will be given in the Appendix.

Nitric acid, in a certain state of concentration, is called "*aquafortis*;" the same appellation is, however, very generally given to all commercial nitric acid, without reference to its strength. A closer distinction is drawn between the acid with 40 per cent. water (specific gravity 1·42, and boiling point 253° F.), which is called "*double aquafortis*," and the acid with two-thirds water, which is that in common use. In these different degrees of concentration, the acid is used for many different purposes in the arts, particularly for the purification of gold, for etching copper plates, &c.

Theory of its Production.—All the nitric acid of commerce is obtained either from nitrate of potash, or from nitrate of soda, by means of sulphuric acid. The former, or ordinary saltpetre, contains only 53·4 per cent. of anhydrous nitric acid; whilst the latter, or Chili saltpetre, on account of the smaller equivalent of soda, contains 59·6 to 63·1 per cent. In addition to this, Chili saltpetre is the cheaper salt. The sulphuric acid takes possession of the alkali in both cases, and the nitric acid is liberated. It should be borne in mind, that sulphuric acid can unite in two proportions with the alkali; and it is by no means unimportant whether the neutral or the acid sulphate is ultimately formed. Whether 1 or 2 equivalents of acid to 1 of alkali are used, the bisulphate is always produced in the first instance; but, in the former case, with 1 equivalent, the saltpetre is only half decomposed, whilst with 2 equivalents, the decomposition is complete. This will be obvious from the following equation for nitrate of potash:

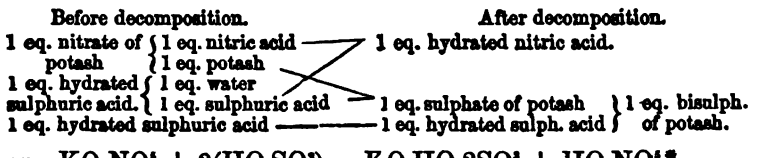
2 equivs. hydrated sulphuric acid $\left\{\begin{matrix}HO.SO^3\\HO.SO^3\end{matrix}\right.$ and $\left.\begin{matrix}KO.NO^5\\KO.NO^5\end{matrix}\right\}$ 2 equivs. saltpetre.

produce:

1 equiv. bisulphate of potash $\left\{\begin{matrix}KO.SO^3\\HO.SO^3\end{matrix}\right.$ and $\begin{matrix}HO.NO^5 = 1\text{ equiv. hydrated nitric acid.}\\KO.NO^5 = 1\text{ equiv. (undecomposed) saltpetre.}\end{matrix}$

The one-half only of the producible nitric acid is consequently obtained, and this distils over at a temperature of 132° C. (270° F.). If the temperature be raised still higher, a second decomposition ensues, the second portion of saltpetre being forced, by the action of the bisulphate of potash, to relinquish its nitric acid. This acid, however, cannot resist the influence of the high temperature, and is resolved into oxygen and peroxide of nitrogen, which dissolves in the hydrated nitric acid already distilled, and forms *fuming* nitric acid. It has been found, when Chili saltpetre and 1 equivalent of sulphuric acid are employed, that the temperature at which the second equivalent of nitric acid separates, is not nearly so high; so that only a portion of it is decomposed, and, instead of fuming acid, a coloured acid is obtained, which, by dilution with water, and a slight application of heat, may be easily freed from all peroxide of nitrogen, and converted into ordinary nitric acid. This constitutes a third advantage attending the use of Chili saltpetre for the manufacture of nitric acid: the greater cheapness of the salt, and its larger percentage of acid have already been mentioned.

With ordinary saltpetre, 2 equivalents of sulphuric acid are, therefore, absolutely necessary; and the decomposition occurs as follows:


Before decomposition.
After decomposition.
1 eq. nitrate of potash
1 eq. nitric acid
1 eq. potash
1 eq. hydrated sulphuric acid.
1 eq. water
1 eq. sulphuric acid
1 eq. hydrated nitric acid.
1 eq. sulphate of potash
1 eq. hydrated sulphuric acid
1 eq. hydrated sulph. acid
1 eq. bisulph. of potash.

or: $KO.NO^5 + 2(HO.SO^3) = KO.HO.2SO^3 + HO.NO^5$*

nitrate of potash. — sulphuric acid. — bisulphate of potash. — nitric acid.

Adopting these proportions, which correspond with 96 to 97 parts of oil of vitriol to 100 parts of nitrate of potash, the whole of the nitric acid is obtained, and, according to calculation, 100 parts of nitre ought to produce 62·25 nitric acid; somewhat more is in fact obtained, for the oil of vitriol contains rather more water than the proportion corresponding with the hydrate, and the saltpetre is always more or less damp, so that sufficient water passes

* The action is precisely analogous to that which takes place in the preparation of hydrochloric acid by decomposing common salt with sulphuric acid, and, in short, in every case of the decomposition of a salt of a monobasic acid by a bi-basic acid (see HYDROCHLORIC ACID, Part III., p. 339).

off to produce the second hydrate of nitric acid. It is not desirable to dilute the sulphuric acid, as the oil of vitriol contains the quantity of water required to form bisulphate of potash and nitric acid. This, however, is not the case when Chili saltpetre is used with 2 equivalents of sulphuric acid; for bisulphate of soda unites with 3 equivalents of water, and these it must obtain from the nitric acid, which is consequently decomposed. Water must, therefore, be added in this case; and the proportions best suited to prevent any overflow during ebullition, are: 100 Chili saltpetre to 117 oil of vitriol and 30 of water. The production of bisulphate of soda being in this case unnecessary, as was previously stated, the simple proportions of 58 oil of vitriol to 100 of Chili saltpetre may also be substituted for those above.

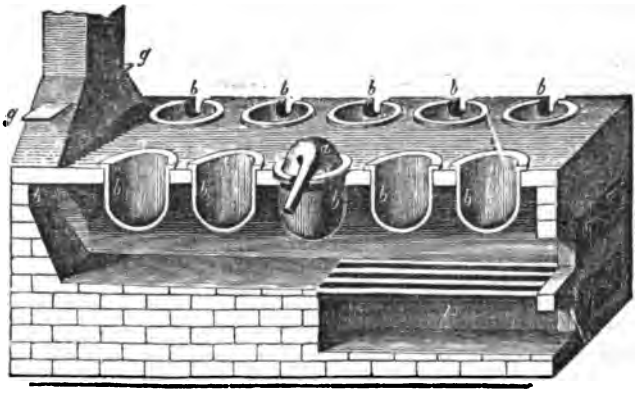
In consequence of the high price of oil of vitriol, clay was employed in former times, and at a later period green vitriol (see p. 351). In the former case, the silica in the clay effected the decomposition; but, as the necessary quantity of water was not supplied to give stability to the acid, a great portion of it was lost by decomposition. The same occurred with green vitriol, the nitric acid being derived from the nitrate of iron first produced, and undergoing decomposition at a high temperature.

DISTILLATION OF NITRIC ACID.

In the manufactories of aquafortis, glass or earthenware retorts are used, or vessels of cast-iron.

The retorts, *a*, are sunk in sand-pots, *b b b*. The sand-pots are placed in a row in a so-called galley-furnace (*Galereenofen*) Fig. 145. A furnace of this kind is built with two fire-places

FIG. 145.



working into a common chimney, the damper of which is seen at *g*, separated by a thin partition. Above the ash-pit, *l*, is the grate *o*, whence the flame traverses the whole length of the furnace, heats the five sand-pots, and escapes into the chimney at *h*. The pots can be removed and replaced at pleasure, and the fire so regulated as to communicate a uniform heat to the pots. On charging the retorts, great care is necessary to prevent any saltpetre or sulphuric acid from remaining in the necks, as these substances, if not removed, would be carried into the receiver with the acid. The saltpetre which remains attached, is shaken into the retort by gentle tapping, and the sulphuric acid is introduced by a long-necked funnel. The receiver should be kept cool by a stream of cold water; but, as this is too troublesome, the use of water is usually dispensed with, and a very large receiver is employed, to expose an extensive surface to the cooling action of the air. When the charge begins to get warm, an empty receiver is applied, as the first portions of acid are very impure, and mixed with red vapours, arising, partly, from the decomposition of a portion of nitric acid by dust and organic matter, which is always present, but chiefly from the dehydrating action of the sulphuric acid. At the moment when the first portions of nitric acid are evolved, the whole of the sulphuric acid is not in contact with saltpetre; a portion is consequently free, and this portion takes water from the nitric acid, and converts it into oxygen and peroxide of nitrogen. Another source of impurity is found in the chlorides of sodium and potassium contained in the nitre, which evolve hydrochloric acid when acted on by sulphuric acid. This reacts upon the nitric acid, producing chlorine, nitric oxide (which, with the air in the retort forms the red vapours of peroxide of nitrogen) and water. The hydrate of nitric acid is decomposed to a slight extent by mere distillation, with evolution of red fumes, which are never entirely absent, but become almost imperceptible soon after the commencement of the operation. At this period of the distillation, the receiver with the impure acid is exchanged for another, containing as much water as is required to bring the acid to the proper strength (40 per cent. of the saltpetre for acid of 1·4 specific gravity). The heat must be cautiously applied at first, as the contents of the retort swell, and threaten to overflow. The pasty mass afterwards sinks down, and boils steadily at a temperature of 132° C. (270° F.), with constant evolution of nitric acid. Towards the end, when the mass has

become very stiff, and the heat can no longer permeate it uniformly, the sides of the retort become overheated, and cause the re-appearance of ruddy fumes. The distillation should now be stopped, for very little more nitric acid passes over, even when the residue is brought into a state of fusion; and at this period it can be most easily removed from the retort.

The use of iron vessels was first introduced in France, and their form and mode of arrangement are similar to those adopted in the production of hydrochloric acid, when this is made the object of a special manufacture, and not obtained as a waste product.

The decomposing vessels are cast-iron cylinders—retorts with movable lids, which are closed in the same manner as gas retorts. Each pair of retorts is fixed over a common fire-grate, of which one surface contains several (Figs. 146 and 147), and is surrounded

FIG. 146.

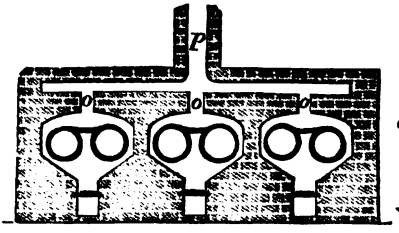
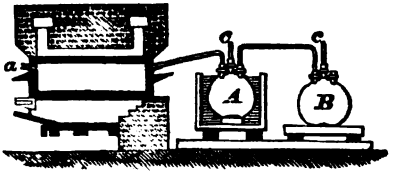


FIG. 147.



by the flame which, reverberating in the dome, escapes by the flues *o*, to the common horizontal channel *p*, and thence to the chimney. The cover of each retort is supplied with a mouth-piece; the hinder lid and its aperture, situated above the door of the furnace, is used for the introduction of the sulphuric acid; the front mouth-piece, or aperture, conveys the acid, by means of a tube, to the three-necked earthenware receivers, *A* and *B*. The tube must be of glass, that the colour of the vapours may be observed, unless glass vessels are employed as receivers. A better construction consists in making the front lid of the retort in one piece; the vapours are then carried off by an earthenware tube, fitting into an aperture in the top of the retort, just behind the lid, and connected by a bent glass tube with the first condensing vessel. (See figure 153, p. 347.) By this arrangement the contents of the retort are less likely to be carried over into the condenser at the beginning of the process, when the action is rather violent.

The cylinders are adapted for 170 lbs. of saltpetre; as soon as they are charged, the covers and tubes are luted on,* and the sulphuric acid is poured into the aperture *a*, which is then immediately closed. The fire must be regulated in a slow and uniform manner; the greater part of the acid is condensed in the first receiver, which is placed in cold water; whatever escapes from this vessel is condensed in *B*. Safety-tubes are inserted at *c c*, to prevent any accidents which might be caused by the atmospheric pressure, in consequence of too great condensation towards the end, and in order that the air may escape in the beginning.

With an apparatus of this description, much acid may be obtained in a short time; it is, however, less pure, and accompanied by a greater quantity of the ruddy fumes, and the cast-iron, particularly in the colder parts, is somewhat attacked by the acid. This occasions a loss of acid, and at the same time, a constant demand for new retorts.

As the upper part of the retorts is most exposed to the action of the acid fumes, the lower part being protected by the fused saline mass, some manufacturers turn them round, from time to time, so as not always to expose the same part of their surface to the corroding vapours. To save this trouble, retorts are sometimes used, formed of two halves, fitting one into the other. The upper half is lined with an arch of bricks set edgeways, which protects it perfectly. The junction of the two half-cylinders is lined with lead, which melts during the distillation, and forms an air-tight joint. As, however, this method of joining is not always secure, many manufacturers use cylinders cast in one piece, but having their upper half of a longer radius than the lower (Fig. 148). The upper half of the cylinder is lined with bricks in the manner above described.

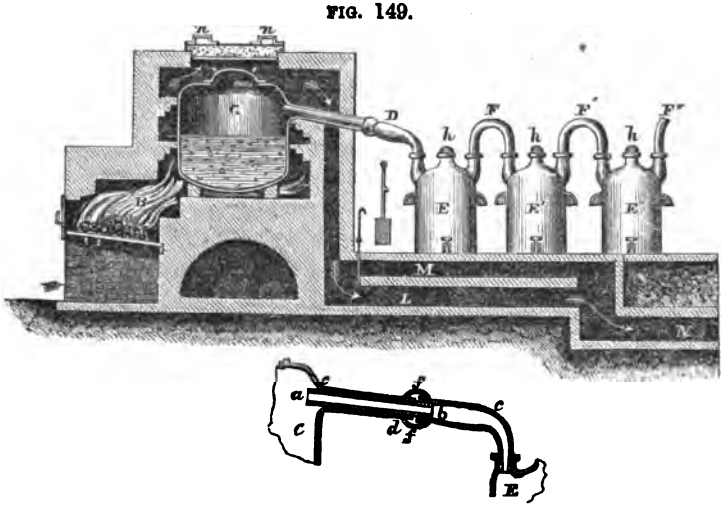
FIG. 148.

At the present day, many French manufacturers prefer the form of apparatus represented in Figure 149.

C is a cast-iron boiler, 1·33 metre in diameter, 1 metre deep, and having a large aperture at the top, which can be closed with a lid. The boiler is charged with 250 kilogrammes of nitrate of soda and 288 kilogrammes of sulphuric acid at 66° Baumé, or 300 kilogrammes at 60°. The lid is well luted with a mixture of

* The lute is formed of clay, linseed oil, and a small proportion of oil-cake meal, and may be used long and repeatedly.

FIG. 149.



clay and sand; and, the fire having been lighted, the furnace is closed at top by the cast-iron plate *n n*.

The boiler is connected with the condensers by means of a wide iron tube, *c d*, protected against the action of the vapours by an earthenware lining, luted to it by a layer of fine crucible-clay. The lining passes beyond the iron tube by 3 centimetres within and 10 centimetres without, and its outer extremity is inserted into a glass adapter, D, united to it by a fine luting. The other end of the adapter passes into the first tubulure of an earthenware Woulfe's bottle, E, capable of holding from 200 to 250 litres, and having a cock at the lower part, for drawing off the acid. The small tubulure, *h*, serves for pouring in water (to bring the acid to the strength of 36° Baumé when required) for gauging the depth of liquid in the bottles, &c. The acid not condensed in the vessel E, passes on through a series of 10 or 12 similar vessels, E′, E″, &c.

The boiler is heated by the fire, A B. The flame and gaseous products of the combustion, enveloping it on all sides, and even passing between the lid of the boiler and the top of the furnace, keep the metal at a high temperature, which protects it from the action of the acid vapours. The products of combustion then re-descend into the double flue, L M, provided with a damper, which, when lowered, completely closes the lower

flue, L, causing the smoke and heated gases to pass through the upper flue, M. This flue, passing under the first two condensers E, E′, heats them, and thus prevents their fracture, which would otherwise ensue from the dropping of the boiling acid on the cold earthenware. As soon as these vessels are sufficiently heated, and a layer of liquid has condensed in each of them, the damper is raised, so as to shut the flue M and open L, causing the gases to pass through the latter. In either case, the products of combustion pass onwards into the common flue, N, terminating in the vertical chimney which carries away the smoke of the entire apparatus.

With this apparatus and the quantities of material above-mentioned, the disengagement of colourless, or nearly colourless, nitric acid (p. 341) lasts for about twelve hours. When the distillation is quite finished, the cover, *n n*, of the furnace is raised by a chain and pulleys, or, better, by a revolving crane; the lid of the boiler is then raised, and two diametral channels, cutting one another at right angles, are made, by means of an iron bar, in the still soft mass of sulphate of soda. The contraction which takes place on cooling, causes the four segments thus formed to detach themselves from each other, so that they can be easily taken out with iron tongs.

Fractionation of the products.—The nitric acid collected in the first two condensers, E, E′, is strong enough for sale; that of the other vessels, in which water has been placed to assist the condensation, is too weak: it is drawn off by the cocks and poured into the first and second bottles, so as to bring the acid to the strength of 36°, 38°, or 40° Baumé, as desired. If the mono-hydrated acid, $NO^5.HO$ or NO^4H, is required, water is poured into the last vessel only, the acid condensed in this vessel being then used, as above, for preparing the weaker acids of commerce.

Decoloration of the product.—Nitric acid obtained by either of the processes above described, is always coloured with peroxide of nitrogen. It may be decolorized by heating it in vessels kept at a temperature of 80° or 85° C. in a water-bath, till it no longer gives off red vapours. The vapours thus evolved may be utilized by directing them through tubes of glass or earthenware into sulphuric acid chambers.

The fuming (mono-hydrated) acid is most easily decolorized by

heating it gently in a flask or retort, and passing a stream of dry air through it (A. Smith).*

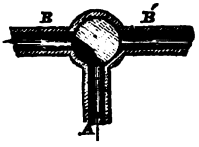
Improved Methods of Condensation.

Two important modifications have been made in the apparatus used for condensing the nitric acid. The first, which is in use at the factory of M. Chevé, has for its object the direct preparation of colourless acid; the second, invented by MM. Devers and Plisson, is intended to condense the vapours more completely, and to save labour in the management of the apparatus.

1. *Direct preparation of colourless Nitric Acid.*—It has already been observed, that the red vapours of peroxide of nitrogen are produced by decomposition of the nitric acid, chiefly towards the beginning and end of the distillation. Hence, by collecting apart the acid which passes over in the intermediate stage of the process, a colourless product will be at once obtained. This may be effected by means of a three-way cock working in an earthenware T-tube (Figs. 150 and 151), the straight branch, A, of which is connected with the generating vessel, while each

FIG. 150.

FIG. 151.

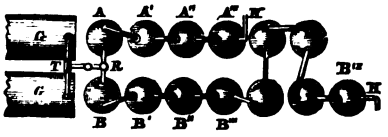


of the two other branches, B, B′, communicates with a separate series of condensing vessels. The cock is perforated in such a manner that, by turning it one way, a communication is established between the branch A, connected with the generating vessel, and the branch B, leading to one series of condensers, while the communication between A and the other branch, B′, is shut off.

Fig. 152 exhibits an arrangement of two series of condensers for collecting apart the coloured and colourless portions of acid. The vapours proceeding from the two cylinders are conveyed by the T-tube to the cock R, one branch of which communicates with a series of four carboys, A, A′, A″, A‴, destined to receive the

* "Memoirs and Proceedings of the Chemical Society," Part III., p. 399.

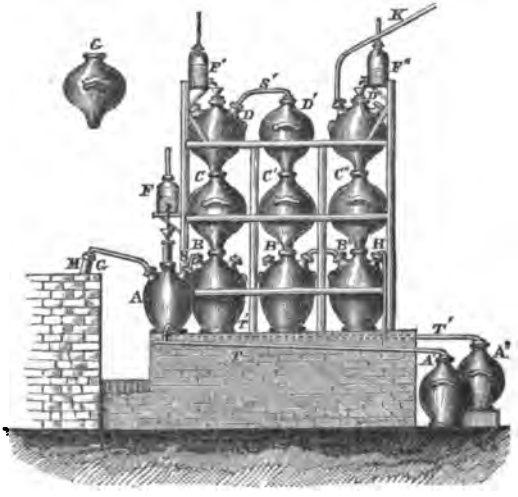
FIG. 152.



colourless acid, while the other communicates with a series of nine carboys, B, B′, B″, ... B^x, in which the coloured acid is condensed. The carboys are connected together by bent glass tubes, as shown in the figure; and to the last of each series is attached a glass tube, N, N′, by which the uncondensed vapours are conveyed into the chimney of the factory. At the commencement of the distillation, the communication with the series of nine carboys, B, is opened, and kept open as long as the vapours passing through the glass tubes appear red; but, as soon as they become colourless, the cock is turned, so as to shut off the connection of the generators with the carboys B, and admit the vapours into the four carboys, A. By this means, colourless acid is at once obtained, ready for sale, without the trouble of decoloration.

2. *Devers and Plisson's Condensing Apparatus.*—This apparatus (Fig. 154) consists of a series of ten carboys, arranged in three rows one above the other. Six of them are open at the bottom and terminate in funnels which fit into the mouths of those immediately below them; one of these vessels is represented separately at G (Fig. 153). M (Fig 154) is an earthenware tube

FIG. 153. FIG. 154.

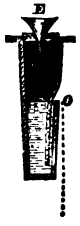


proceeding from one of the generating cylinders (p. 342), and connected, by a bent glass tube, with one of the tubulures of the first condensing vessel, A, which receives the first portions of acid and any impurities that may pass over with them in consequence of the action in the cylinder becoming too violent. From the lower part of this bottle, shown in section in Figure 155, proceeds a small siphon-tube T, having a lateral aperture, L, below the level of the external opening, *o*, so that, when the level of the liquid within the vessel rises above *o*, the surplus flows out into the inclined tube T (Fig. 154), which conveys it into the receiver A, but ceases to run as soon as the surface falls to the level of *o*, the arrangement thus forming a complete water-joint.

FIG. 155.

Into the middle tubulure of the bottle, A, is fitted a siphon-funnel (shown in detail in Figure 156), through which water is supplied from the bottle F to A, to assist the condensation and reduce the acid to the required strength. It is clear from the construction, that the water will run out at *o* as long as the level within the siphon is above *o*, but no longer, so that this apparatus likewise forms a complete water-joint.

FIG. 156.



Into the third tubulure of A (Fig. 154) is fitted a bent glass tube, S, which conveys the uncondensed vapours into the bottle, B, likewise provided with a discharge-tube forming a water-joint, and discharging its contents—as do also the other two vessels, B′, B″, into the inclined tube, T′ (shown in the figure by dotted lines), and ultimately into the receiver A″. The vapours which escape condensation in B, pass upwards into C, and thence into D, these three vessels communicating freely by their lower parts. The large cooling surface which the vapours meet with in these two bottles, C, D, causes a portion of them to condense, the resulting liquid running back into B, and being thence discharged into A″. The still uncondensed vapour passes through the glass tube S′ into D′, thence into C′ and B′, where the condensed portions are arrested, and whence they pass through the tube T′ into A″; while the non-condensed portion is carried through the tube S″ into the series of condensers B″, C″, D″. From this last bottle, D″, the uncondensable vapours escape by the tube K into the chimney, after passing through an earthenware worm-tube, down which a thin stream of water is made to flow in the contrary direction. F

and F″ are two bottles which, together with F, supply the quantity of water required to reduce the density of the acid to 36°. To avoid pressure in the bottles A′, A″, a tube H, and a corresponding tube H′ (not shown in the figure), are attached to the inclined tubes T, T′, for the purpose of conducting the uncondensed vapours into the bottle B″, where they are united with those proceeding from the other parts of the apparatus.

The result of the whole arrangement,—which, though somewhat complicated in appearance, is very easy to work,—is, that the acid vapours are first condensed in the bottle A, which conducts them into a special receiver A′—a very useful precaution, inasmuch as the portions first condensed are generally impure—then into the bottles B, B′, B″, whence the liquid product runs off into a common receiver, A″.

The advantages of this mode of condensation are considerable. The apparatus, once mounted, may remain in action for a fortnight, or even a month, without being taken to pieces; so that the daily emptying and reluting of the condensers, which is required with the ordinary apparatus, is dispensed with—and a great saving of labour, as well as of material for luting, is effected. Moreover, the vapours, in their long circuit through the condensers, meet with a very large cooling surface, which greatly facilitates the condensation. MM. Devers and Plisson have found, by comparative experiments, that 100 parts of nitrate of soda and 120 parts of sulphuric acid of 120° Baumé, yield, with their apparatus, 126 parts of nitric acid of 36° Baumé, whereas, with the ordinary condensing apparatus, the same quantities of material yield only 120 parts.

Purification of Commercial Nitric Acid.

Ordinary nitric acid is frequently contaminated with peroxide of nitrogen or nitrous acid, which gives it a red or yellow colour; with hydrochloric acid, arising from the presence of chlorine in the nitrate from which it has been distilled; and with sulphuric acid, carried over from the generating vessel by spirting or by too rapid distillation. The greater part of the peroxide of nitrogen may be expelled by boiling the acid for a short time in a retort, the peroxide of nitrogen then passing over with the first portions of the distillate (p. 345). A more effectual method of removal, is to heat the coloured acid gently with a small quantity of urea, which completely decomposes the peroxide of nitrogen (Millon). To get rid of the hydrochloric and sulphuric acids, the impure nitric acid is

redistilled; the first fourth of the distillate, which contains all the hydrochloric acid, is rejected; and the second and third fourths are collected as pure nitric acid; while the sulphuric acid remains in the retort with the last fourth of the nitric acid. If the nitric acid, after this treatment, should still contain hydrochloric acid, it must be distilled once more, with an addition of a small quantity of nitrate of silver.

Nitric acid prepared from Chili saltpetre often contains iodine. Such acid, when distilled with sulphuric acid, yields a sublimate of iodine after all the nitric acid has passed over. The iodine (which is in the form of iodic acid) may also be detected by reducing it with sulphuretted hydrogen or hyposulphite of soda, and then testing with starch.

Non-volatile impurities, chiefly potash- or soda-salts, are occasionally present in the acid, having been carried over by too rapid distillation.

Special Modes of Preparation.

The following new methods of manufacturing nitric acid are described by F. Kuhlmann.*

A. *By the action of Chloride of Manganese on Nitrate of Soda.*—When protochloride of manganese is heated with nitrate of soda to 230° C., a large quantity of nitric acid or of condensable nitrous fumes is evolved; and an oxide of manganese is formed, sufficiently rich in oxygen to serve again for the evolution of chlorine. The reaction may be represented by the equation:

$$5MnCl + 5(NaO.NO^5) = \left\{ \begin{matrix} 2Mn^2O^3.MnO^2 \\ \text{or } 3MnO^2.2MnO \end{matrix} \right\} + 5NaCl + 5NO^4 + 2O.$$

The mixture of peroxide of nitrogen and oxygen, coming in contact with water in the condenser, is converted into nitric acid; and the excess of peroxide of nitrogen is resolved into nitric acid and binoxide of nitrogen ($3NO^4 = 2NO^5 + NO^2$). If the apparatus contains a quantity of air sufficient to reconvert the whole of the binoxide of nitrogen, thus produced, into peroxide, this reaction is repeated; if not, part of the nitric oxide dissolves in the nitric acid, and the rest escapes into the air. 100 parts of nitrate of soda yield by this process from 125 to 126 parts of nitric acid of 36° Baumé, that is to say, nearly as much as by the ordinary

* Compt. rend., lv, 246; Rép. Chim. app. 1862, p. 337; Wagner's 'Jahresbericht,' 1862, p. 239.

process. Other chlorides, especially the chlorides of calcium, magnesium, and zinc, yield in like manner nitric acid and chloride of sodium, together with lime, magnesia or oxide of zinc.

B. *Action of certain Sulphates on Alkaline Nitrates.*—All sulphates, even those which are very permanent, and do not play the part of acids, are capable of decomposing the nitrates of the alkalies. Sulphate of manganese decomposes nitrate of soda, yielding products similar to those which are obtained when chloride of manganese is used, sulphate of soda being produced instead of chloride of sodium, and the quantity of nitric acid obtained being nearly the same as that produced in the above-described reaction with the chloride. Similar reactions take place with the sulphates of zinc and magnesia, and even with sulphate of lime.

This last-mentioned reaction affords, to a certain extent, a *direct application* of the sulphuric acid of gypsum; but as it requires rather a high temperature, it yields only about 30 per cent. of the weight of the nitrate of soda in acid of 35°: the residue is a mixture of lime and sulphate of soda.

C. *Action of certain Metallic Oxides, Alumina, and Silicic acid on Nitrates.*—Wöhler has shown, that, when a mixture of peroxide of manganese and nitrate of soda is moderately heated out of contact with the air, caustic soda is formed, but no salt of manganic acid. Kuhlmann finds that an oxide of manganese containing a smaller amount of oxygen, *e. g.*, 42 per cent., mixed with nitrate of soda, facilitates its decomposition by heat, yielding a quantity of nitric acid equal to between 70 and 90 per cent. of the nitrate of soda; whereas nitrate of soda heated alone, yields only from 10 to 15 per cent. of nitric acid. As peroxide of manganese has not the same tendency to take oxygen from the nitrate of soda, it does not induce this decomposition so easily. On the other hand, where protoxide of manganese is used, the yield of nitric acid is diminished, because too large a proportion of the oxygen of the nitrate of soda is taken up by the manganese.

De Luna,* by heating to redness a mixture of 2 parts crystallized or $1\frac{1}{4}$ parts slightly-dried sulphate of magnesia, and 1 part of nitrate of potash or nitrate of soda, obtained nitric acid containing a considerable quantity of nitrous acid; the residue,—consisting of a double sulphate of potash or soda and magnesia, 200

* Compt. rend., xli, 95.

grammes calcined nitrate of soda, and 400 grammes crystallized sulphate of magnesia,—yielded 90 grammes of nitric acid of 40° Baumé (specific gravity 1·384), which, on redistillation, yielded a colourless and perfectly pure acid of 46° Baumé (specific gravity 1·468).

Kuhlmann* recommends the preparation of weak nitric acid, without distillation, by decomposing a strong solution of nitrate of baryta (obtained by decomposing nitrate of soda with chloride of barium) with an equivalent quantity of sulphuric acid. The aqueous nitric acid, decanted from the precipitated sulphate of baryta, has a strength of 10° or 11° Baumé (specific gravity 1·075—1·083), and may be concentrated by boiling to 25° Baumé (specific gravity 1·210).

Preparation of Fuming Nitric Acid.

The usual method of obtaining this acid is, to distil 1 equivalent of saltpetre with 1 equivalent of sulphuric acid, so as to obtain a residue of neutral sulphate of potash (p. 339), a considerable portion of the evolved nitric acid being then decomposed by the high degree of heat to which the materials are raised towards the end of the process.

The red fuming acid may, however, be more easily obtained by using the ordinary proportions of the ingredients (1 equivalent of nitrate to 2 equivalents of sulphuric acid), and adding a substance capable of reducing the nitric acid to the state of nitrous acid or peroxide of nitrogen: the red acid is then obtained from the very beginning of the process. Sulphur may be used for this purpose; but a small portion of the sulphuric acid formed by its oxidation, generally passes over with the nitric acid, and must afterwards be removed by rectification. The following is a better method:—

100 parts of nitre are triturated with 3½ parts of *starch*, and the mixture is introduced into a retort, and covered with 100 parts of sulphuric acid of specific gravity 1·85. The beak of the retort is inserted, without luting, into a glass tube 3 or 4 feet long, the further end of which passes into an ordinary tubulated receiver, which is kept very cool. The distillation begins without external application of heat, requiring only very gentle warming towards the end; 100 parts of saltpetre yield by this process about

* Compt. rend., xlvii, 464 and 675.

60 parts of deep red fuming nitric acid. It is best to fill the retort only to about one-third.—Brunner.*

Uses of Nitric Acid.

The applications of nitric acid in the arts and manufactures depend:—1. On its oxidizing and solvent powers; 2. On its substituting action. The more dilute acid acts for the most part in the former of these modes; the most highly concentrated acid, in the latter.

1. All metals, except gold, platinum, and some of the rarer metals, are oxidized, and the greater number are dissolved, by nitric acid. In these reactions, the metal is oxidized at the expense of a portion of the nitric acid, which is thereby reduced to a lower oxide of nitrogen, generally the binoxide; and the oxide, thus formed, dissolves in the remainder of the acid, in the form of a nitrate; thus, with copper:—

$$3Cu + 4(NO^5.HO) = 3(NO^5.CuO) + NO^2 + 4HO.$$

On this mode of action depends the preparation of the nitrates of copper, lead, mercury, and silver,—also the etching of copper-plates for engraving, the cleansing of copper and bronze, the refining and assaying of gold and silver, and numerous analytical processes connected with manufactures. Nitric acid mixed with hydrochloric acid, forms *nitro-muriatic acid*, or *aqua regia*, used for dissolving gold, platinum, and other metals and alloys not attacked by either acid alone.

Many organic substances are likewise oxidized by nitric acid, often with great violence, a variety of products being formed, the most frequent of which are oxalic acid and picric or carbazotic acid.

2. The strongest nitric acid (NO^6H), of specific gravity 1·522, acts on organic bodies for the most part in a different manner, removing part of the hydrogen of the organic compound in the form of water, and introducing in its place an equivalent quantity of the radical nitryl, NO^4. The industrial application of this mode of action is of comparatively recent date, but is becoming of daily increasing importance. The most important products obtained by it are:—

a. Nitrobenzol, now largely consumed in the manufacture of aniline; used also in perfumery as artificial oil of bitter almonds.

* Dingl. pol. J., clix, 385; Rép. Chim. app., iii, 188.

It is obtained by the action of monohydrated nitric acid on benzol, as represented by the equation :—

$$C^{12}H^6 + NO^4H = C^{12}H^5(NO^4) + 2HO.$$

Benzol. Nitric acid. Nitro-benzol.

b. Picric acid, which forms a valuable yellow dye, is obtained in like manner from phenol or carbolic acid :

$$C^{12}H^6O^2 + 3NO^4H = C^{12}H^3(NO^4)^3O^2 + 6HO.$$

Phenol. Nitric acid. Picric acid.

c. Gun-cotton, prepared by immersing cotton-wool in a mixture of strong nitric and sulphuric acids, consists of woody fibre or cellulose ($C^{12}H^{10}O^{10}$), in which the hydrogen is more or less replaced by an equivalent quantity of NO^4.

Xyloïdin from starch, and *nitroglycerin* from glycerin, are formed in a similar manner.

d. Fulminating silver and *fulminating mercury*, produced by boiling these metals in a mixture of nitric acid and alcohol, also belong to this head, inasmuch as they have both the composition and the character of nitro-compounds.*

DETECTION AND ESTIMATION OF NITRIC ACID.

All nitrates—excepting a few basic salts—are easily soluble in water : hence nitric acid cannot be precipitated from its solutions as an insoluble salt, but must be detected and estimated by other methods.

a. DETECTION.—1. When free nitric acid is mixed with an excess of a solution of a *protosalt of iron*, the nitric acid gives up 3 equivalents of oxygen, converting the protosalt of iron into a sesqui-salt, and is itself reduced to binoxide of nitrogen, which dissolves in the excess of the iron salt, in the cold or at a very gentle heat, imparting to it a dark brown, or if the quantity of nitric acid present is large, a nearly black colour. On boiling the liquid, binoxide of nitrogen is evolved, and the dark colour disappears ; hence, in applying this test for nitric acid, it is indispensable to prevent the temperature of the liquid from rising above a very moderate degree.

Nitric acid, in combination, does not exhibit this reaction. Hence, to detect it in this manner, in a neutral or alkaline solution, the acid must first be set free. For this purpose, the liquid is mixed in a test-tube with about an equal volume of strong sul-

* See Watts's Dictionary of Chemistry, ii, 730.

phuric acid, the mixture left to cool, and a concentrated solution of protosulphate or protochloride of iron cautiously poured upon it, so as to float on its surface. If nitric acid is present in tolerably large quantity, the iron-solution quickly assumes the dark brown colour above mentioned; if only a very small quantity of nitric acid is contained in the liquid, its presence is indicated by the formation of a rose-coloured, purplish-brown, or dark brown ring at the surface of contact of the two liquids. This test is extremely delicate, the merest traces of nitric acid being sufficient to produce a rose-coloured tinge where the two liquids meet. In applying it, care must of course be taken to ensure that the sulphuric acid used is quite free from nitric acid or binoxide of nitrogen, by testing it as above with the solution of the iron salt, without any other addition.

2. *By the formation of Ammonia when Nitric Acid is decomposed by Nascent Hydrogen.*—It has long been known that when nitrate of potash or soda is heated with zinc, water, and excess of potash, ammonia is evolved, its formation arising from the union of the nitrogen contained in the salt, with the hydrogen evolved by the action of the zinc on the potash-solution. This method does not, however, effect a complete decomposition of the nitric acid; and, if applied to a liquid containing only small quantities of that acid, it would not give certain indications. But it may be greatly facilitated and rendered complete, by the introduction of another metal not acted upon by the potash, so as to form a voltaic circuit. Thus, when zinc and iron are placed together in a moderately strong solution of caustic potash, hydrogen is freely disengaged, even without the application of heat, the zinc being oxidized and the hydrogen evolved at the surface of the iron. A similar effect is observed if platinum, copper, or tin be substituted for the iron; but with these metals the action is less energetic. The addition of a nitrate to the liquid, is followed by an immediate evolution of ammonia. To apply this reaction to the detection of nitric acid, the liquid to be examined is reduced to a small bulk and poured into a test-tube, containing 2 or 3 grammes of a mixture of granulated zinc and clean iron-filings. A small quantity (5 or 6 cub. cent.) of strong potash-solution is then added, and the whole is heated to boiling. Ammonia may then be detected at the mouth of the tube by its usual characters, viz. its odour, its alkaline reaction, and the formation of dense white fumes when a rod dipped in dilute hydrochloric acid is held near

the mouth of the tube; 5 milligrammes of nitre, thus treated, give a distinct reaction with reddened litmus. The delicacy of the test may be greatly increased by the use of potassio-iodide of mercury (the solution obtained by adding iodide of potassium to corrosive sublimate till the scarlet precipitate first formed just redissolves), which produces a red or brown precipitate, according to the quantity of ammonia present. The mixture should be gently heated, and the evolved gases passed into a small quantity of dilute hydrochloric acid. The acid solution is then to be supersaturated with potash, and tested with a drop of potassio-iodide of mercury; 0·001, 0·0005, and even 0·0001 gramme of nitre, thus treated, gives a distinct red coloration (A. Vernon Harcourt, *Chem. Soc. J.*, xv, 381). Schulze (*Chem. Centralblatt*, No. 53) proceeds in a similar manner, but uses platinized zinc in place of the mixture of zinc and iron.

This method—which may be used also for the quantitative estimation of nitric acid (p. 368) serves to distinguish that acid from all others excepting nitrous acid.

3. *By the reaction of Nitric Acid with Phenyl-compounds.*—Strong nitric acid converts phenol (or carbolic acid) into reddish brown nitro-phenol. To apply this reaction to the detection of nitric acid, 1 part of phenol is dissolved in 4 parts of strong sulphuric acid, and the solution is diluted with 2 parts of water. The substance to be tested, if in solution, is evaporated on a porcelain crucible, or its cover; and a drop or two of the phenyl-sulphuric acid is allowed to fall upon it at a temperature of about 100° C. If nitric acid is present, a reddish-brown colour is immediately produced. This test is said to be more delicate than that with protosulphate of iron, having given a distinct indication of the presence of nitric acid in the residue of a drop of water not containing more than 0·000006 gramme of iron, whereas four such drops were not sufficient to give a perceptible indication with the iron test. If organic matters, or compounds of chlorine, bromine, or iodine are likewise present, from which sulphuric acid would separate carbon or the haloïds, it is best to add a drop or two of strong ammonia to the coloured product, when the haloïds will be dissolved in the form of colourless salts, and the carbon will remain suspended in small particles, not interfering with the recognition of the characteristic yellow colour of nitro-phenylate of ammonia (H. Sprengel, *Chem. Soc. J.*, xvi, 396).

4. *By reduction with Copper.*—Nitric acid in the free state

and all nitrates when mixed with sulphuric acid, evolve red fumes in contact with copper-turnings or filings, the nitric acid being reduced to binoxide of nitrogen, which, on coming in contact with the air, is converted into the red peroxide. The application of a gentle heat facilitates the reaction, and at the same time deepens the colour of the peroxide of nitrogen. When only a small quantity of nitric acid is present, it is best to introduce the materials into a long test-tube and look down it: the colour of the peroxide then becomes visible. This reaction also distinguishes nitric acid from all others, except nitrous acid and hydrobromic acid. The salts of the latter give off red fumes of bromine when treated with sulphuric acid alone; but they are easily distinguished from nitrates by the precipitate which they form with nitrate of silver.

5. *By the formation of Nitroprussides, and the reaction of these salts with Alkaline Sulphides.*—The substance to be tested is mixed with a few drops of a strong solution of *ferrocyanide of potassium* (yellow prussiate), then with a small quantity of hydrochloric acid; and the liquid is heated to 71° C. and slightly supersaturated, on cooling, with an alkaline carbonate. If nitric acid was originally present, the filtered liquid, when mixed with a drop or two of solution of sulphide of ammonium or any other alkaline sulphide, exhibits a transient purple or violet colour, sufficing for the detection of $\frac{1}{1000}$ of a grain of nitric acid in the substance under examination (E. W. Davy, *Chem. Gaz.* 1850, p. 219). This reaction also, is not produced by any other acid excepting nitrous acid.

6. *By the decoloration of Indigo.*—A solution of indigo in pure sulphuric acid may be boiled for any length of time without changing colour; but on adding any liquid containing free nitric acid not too much diluted, the blue colour of the indigo is destroyed and changed to a pale yellow. If the nitric acid in the liquid to be tested is not in the free state, it must be separated by adding sulphuric acid; or better—sulphuric acid is added in excess to the indigo-solution, and the liquid boiled before adding the substance under examination, in order to ascertain whether the sulphuric acid itself is free from nitric or nitrous acid. If the colour remains unaltered after boiling for some time, the liquid to be tested for nitric acid may then be added.

This reaction is likewise produced by nitrous acid and by the oxygen-acids of chlorine, bromine, or iodine: the latter are easily

distinguished from nitric acid by the residue of metallic chloride, bromide, or iodide which their salts leave when ignited,—also by their reactions with nitrate of silver, and by many other characters.

7. *By the evolution of Chlorine when a Nitrate is heated with Hydrochloric Acid.*—When a nitrate in the solid state is heated with excess of hydrochloric acid, chlorine is abundantly evolved, and may be recognized by its odour and its bleaching powers. To detect the presence of a small quantity of nitric acid, free or combined, in solution, hydrochloric acid is added, and then a few small pieces of gold-leaf, and the liquid is gently heated. If nitric acid is present, the gold dissolves wholly or partially, and the liquid acquires a yellow colour. If the gold does not appear to dissolve after a while, it must be taken out, and the liquid tested with *protochloride of tin*, which, if a trace of gold has been dissolved, will indicate its presence by the formation of a purple precipitate. This reaction is likewise produced by the oxygen-acids of chlorine, bromine, and iodine.

8. *By ignition with Charcoal-powder.*—Nitrates heated with charcoal powder, or ignited on charcoal before the blow-pipe, cause the charcoal to burn, with vivid deflagration, and leave a residue of carbonate, oxide, or reduced metal, according to the nature of the base with which the nitric acid was combined. Chlorates, bromates, iodates, &c. likewise deflagrate with charcoal; but the residues contain a metallic chloride, bromide, or iodide, in addition to the products just mentioned.

All the reactions above described are exhibited by *nitrous* as well as by nitric acid, and even with greater facility: for the nitrites are more easily decomposable than the nitrates, and nitrous acid, though it contains less oxygen, is a more powerful oxidizing agent than nitric acid. Accordingly, nitrites may be distinguished from nitrates by the following characters:—

(1.) A neutral nitrite mixed with the solution of a *protosalt of iron* instantly produces the brown coloration above described (p. 354), without previous addition of sulphuric acid.

(2.) Neutral nitrites treated at ordinary temperatures with *dilute sulphuric acid*, immediately give off red vapours; whereas pure nitrates, thus treated, give off nothing, or only colourless vapours.

(3.) Liquids containing free nitrous acid, and solutions of alka-

line nitrites mixed with dilute sulphuric acid, instantly decompose *hydrosulphuric acid*, with formation of ammonia and precipitation of sulphur. Pure nitric acid, and solutions of pure nitrates mixed with dilute sulphuric acid, do not produce this effect; but, if nitrate of potash or soda be moderately heated for a short time, and the fused mass then dissolved in water and acidulated with sulphuric acid, the solution thus obtained will give a precipitate of sulphur when mixed with aqueous hydrosulphuric acid. The experiment must be made in the cold, as nitric acid heated with sulphuric acid is always partially reduced to nitrous acid.

(4.) A solution of *permanganate of potash* is not decomposed by neutral nitrites; but, on adding dilute sulphuric acid to the solution, decoloration instantly takes place, an effect not produced by pure nitric acid. This reaction and the preceding afford the best means of detecting small quantities of nitrous acid mixed with nitric acid.

(5.) A solution of *iodide of potassium* is instantly decomposed, with separation of iodine, by a solution of an alkaline nitrite acidulated with dilute sulphuric, hydrochloric, or even acetic acid. If the liquid be previously mixed with a little starch-paste, very minute traces of nitrous acid may be detected in this manner, by the production of the well-known blue colour of iodide of starch (D. S. Price, *Chem. Soc. Qu. J.*, iv, 251).* It appears from Dr. Price's experiments, that nitric acid free from nitrous acid does not exhibit either this reaction, or the brown coloration with protosalts of iron, or the decoloration of indigo, these effects being produced only after a portion of the nitric acid has been reduced to nitrous acid by warming with sulphuric acid.

(6.) The liquid to be tested is mixed with a few drops of solution of *ferrocyanide of potassium*, not sufficient to colour it perceptibly, and then with a drop of acetic acid; whereupon, if nitrous acid is present, a yellow colour will be produced. This reaction is also said to be very delicate. In applying it, however, to the detection of very minute quantities of nitrites, it is best to make a comparative experiment with pure water and the same quantities of the reagents, since these may produce nearly the

* The use of iodide of potassium for the detection of nitrous acid may lead to erroneous results, inasmuch as the reaction above described may be produced, even without the presence of nitrous acid, in consequence of the ready decomposability of the iodide of potassium and of the hydriodic acid separated from it (*Liebig and Kopp's Jahresbericht*, 1851, p. 626, foot note).

same colour even in pure water (G. Schäffer, *Silliman's Journal* [2], xii, 117).

(7.) Solutions of alkaline nitrites form with *nitrate of silver* a copious white precipitate of nitrite of silver, and precipitate metallic *gold* from a solution of the terchloride.

(8.) Nitrite of potash or soda added to a solution of cobalt, forms, after a while, a bright yellow precipitate of nitrite of cobaltic oxide and potash (or soda), $C^2O^3.3KO.5NO^3$.

QUANTITATIVE ESTIMATION.

I. Gravimetric Methods.

1. *By neutralization with Baryta.*—The quantity of free nitric acid in an aqueous solution may be determined by agitating the liquid with carbonate of baryta till the acid is completely neutralized, then filtering, evaporating to dryness,—taking care not to heat the residue too strongly,—and weighing the dry nitrate of baryta thus obtained: 100 parts of this salt correspond to 41·39 parts, NO^5, and 48·28 parts, HNO^6.

Or, the solution of nitrate of baryta may be decomposed by sulphuric acid, the precipitated sulphate of baryta weighed, and the equivalent quantity of nitric acid thence determined. 100 parts $BaSO^4$ = 46·35 parts NO^5, and 54·08 parts NO^6H.

If the solution of nitric acid is very dilute, so that it decomposes carbonate of baryta but slowly, it is better to neutralize with baryta-water, then pass carbonic acid gas through the liquid, to remove any excess of baryta, filter, and treat the filtered solution of nitrate of baryta as above.

When nitric acid is combined with a base, it may be liberated by distilling a solution of the salt with sulphuric acid, in the proportion of at least 2 equivalents of strong sulphuric acid (HSO^4) to 1 equivalent of the nitrate. The mixture, which should be rather dilute, is distilled from a tubulated retort into a receiver provided with efficient means of condensation, the distillation being carried nearly to dryness. After the residue has cooled, more water is added, and the distillation is repeated with a fresh receiver. The quantity of nitric acid in the united distillates is then determined by neutralization with baryta, as before. The residue in the retort serves for the estimation of the base. With the proportion of sulphuric acid above indicated, and a considerable quantity of water, there is no reason to fear the reduction of any portion of the nitric acid to a lower oxide of nitrogen.

The following methods of separating nitric acid from bases may also be adopted in particular cases.

Nitrates whose bases are precipitated by baryta-water, and are insoluble in excess of that reagent, may be analysed by boiling them, either in the solid state or in solution, with excess of baryta-water, then filtering, removing the excess of baryta by carbonic acid, and determining the quantity of nitrate of baryta in the filtrate as above.

Some nitrates, as those of lead, copper, bismuth, &c., may be decomposed by hydrosulphuric acid, the metal being precipitated as sulphide, care being taken to dilute the solution and not to use a large excess of hydrosulphuric acid: otherwise sulphur may be precipitated, and part of the nitric acid converted into ammonia. The filtrate, containing the whole of the nitric and a small quantity of hydrosulphuric acid, is mixed with baryta-water; a stream of carbonic acid is then passed through it, to precipitate the excess of baryta and expel the hydrosulphuric acid; the liquid again filtered; and the filtered solution of nitrate of baryta treated as above.

In other cases the bases may be precipitated by an alkaline sulphide, best with sulphide of barium. The liquid filtered from the precipitated metallic sulphide then contains nitrate of baryta and excess of sulphide of barium, and may be treated in the manner just described.

From nitrate of baryta, the base may be precipitated by sulphuric acid; from the nitrates of strontia and lime, by sulphuric acid and alcohol. The filtrate is neutralized with baryta-water, dissolved in water, filtered, and the nitric acid determined as above.

From the nitrates of ammonia, potash, soda, lithia, and magnesia, the acid is most easily separated by distillation with sulphuric acid, as already described.

2. *By the loss of weight sustained by Nitrates on ignition.*—All nitrates are decomposed by heat, the nitrogen being wholly, the oxygen sometimes partly and sometimes wholly expelled, and the base remaining either as an oxide or as metal. Silver, palladium, and other noble metals are left in the metallic state when their nitrates are heated to redness; lead, bismuth, copper, cadmium, zinc, nickel, magnesium, and one or two of the rarer metals, remain as protoxides. In the former case, if the salt is anhydrous, the loss of weight sustained on ignition consists of

NO^6, in the latter of NO^4; but in many cases, as with the proto-salts of iron, cobalt, and maganese, the result is complicated by the formation of an oxide of higher degree of oxidation than that which existed in the original salt. The nitrates of the alkaline earths and of the fixed alkalies, part with the whole of their nitric acid when strongly ignited; but the bases can scarcely be prevented from absorbing small quantities of carbonic acid from the air during the process, or as they cool; moreover, these bases, especially the alkalies, attack all vessels in which the ignition can be performed, uniting partly with their substance; hence the amount of acid in these nitrates cannot be conveniently determined by ignition.

According to Schaffgotsch, the amount of acid in a nitrate may be easily determined by igniting a finely pulverized mixture of the salt with anhydrous borax in a platinum crucible, taking care to raise the heat gradually. The loss of weight then gives the amount of anhydrous nitric acid.

Reich estimates the amount of nitric acid in alkaline nitrates by igniting them, mixed with from 4 to 6 times their weight of pounded quartz; the loss of weight then also gives directly the quantity of acid (NO^5). For the details of this and other methods especially adapted to the valuation of saltpetre, see the last chapter (p. 335).

3. *By conversion of Nitrates into Sulphates.*—When a nitrate is heated with excess of sulphuric acid, the whole of the nitric acid is expelled, the base remaining a sulphate. In the case of the stronger bases, viz. the alkalies and alkaline earths, whose sulphates can sustain a red heat without decomposition, this reaction may be employed for the estimation of the nitric acid. The residue must be heated till all the excess of sulphuric acid is driven off, the expulsion of the last portions being facilitated by placing a piece of carbonate of ammonia in the crucible. The residue is a neutral sulphate, from which the quantity of base may be calculated; and this, deducted from the total weight of the anhydrous nitrate, gives the quantity of anhydrous nitric acid. The nitrates of the weaker bases cannot be analysed in this way, because the corresponding sulphates are likewise decomposed by ignition.

4. *By conversion of Nitrates into Chlorides.*—The nitrates of the alkalies and alkaline earths may be converted into neutral chlorides, of perfectly definite composition, by igniting them in a

covered platinum crucible with excess of chloride of ammonium, as long as fumes of sal-ammoniac continue to escape, the operation being repeated till the weight of the residual chloride becomes constant. The quantity of base is then determined by calculation, and from this, the quantity of nitric acid in the salt.

The chlorides of most of the heavy metals suffer partial decomposition when ignited, especially in contact with moisture.

5. By the action of Arsenious Acid.—Nitric acid converts arsenious into arsenic acid, according to the equation,

$$AsO^3 + NO^5 = AsO^5 + NO^2.$$

Hence for every equivalent of arsenic acid produced, 1 equivalent of nitric acid must be decomposed. To apply this reaction to the estimation of nitric acid, the salt to be analysed (which must not contain lime or phosphoric acid) is mixed with three times its weight of arsenious acid; the whole dissolved in strong hydrochloric acid; the solution evaporated to dryness; ammonia added in excess; and the arsenic precipitated by addition of sal-ammoniac and sulphate of magnesia, as *ammonio-magnesian arseniate*, which, when dried at 100° C., has the composition,

$$(NH^4)Mg^2AsO^6.HO.$$

From the weight of this salt, the amount of nitric acid is calculated by the proportion,

$$(NH^4)Mg^2AsO^6.HO : NO^5 = 189 : 54.$$

Estimation of Water in Nitrates.

In the hydrated nitrates of the stronger bases, the amount of water is easily determined by heating them to 100° C., the water being then completely expelled without any loss of acid. But the nitrates of the weaker bases cannot bear this temperature without decomposition; and in these the water must be determined at the same time as the nitrogen, by igniting the nitrate in a combustion-tube, at the open end of which is placed a quantity of copper turnings, and attaching to the combustion-tube a drying tube containing chloride of calcium, in the same manner as for organic analysis. On heating the tube, the water and nitric acid are driven off; the water collects in the chloride of calcium tube, the increase of weight of which determines its quantity; and the nitric acid is reduced by the red-hot copper to pure nitrogen, which passes on, and may be collected over mercury and measured (see p. 366).

Separation of Nitrates from Chlorides.

All chlorides containing metals which form insoluble phosphates, may be separated from nitrates, by heating the solution containing them, with phosphate of silver. A trace of that salt, which remains in solution, may be easily determined, and in some cases separated, by means of alcohol. Lassaigne has employed this method for separating the chlorides of magnesium and calcium from the corresponding nitrates in well-waters.

In some cases, carbonate of silver is a more convenient precipitant than the phosphate, especially for separating the chlorides of the alkaline earth-metals and of magnesium from the corresponding nitrates. In other cases, however, the carbonate cannot be used, because a great number of oxides are precipitated by it.

The chlorides of the alkali-metals cannot be separated from the nitrates by this method, because the phosphates of those bases are soluble. The method most generally adopted for estimating the quantity of chlorides contained in alkaline nitrates, especially in crude saltpetre, is to precipitate the chlorine by nitrate of silver, and determine its amount, either by collecting and weighing the precipitate, or by the volumetric method with chromate of potash, described at page 425, Part III. of this volume.

II. Volumetric Methods.

1. *By neutralization with Standard Alkaline solutions* (Violette's method).—To determine the centesimal strength of nitric acid, by this process, the value of e in the general formula given in page 118, Part III., of this volume, must be replaced by 63, the equivalent of monohydrated nitric acid, $NO^5.HO$; the formula then becomes

$$T = 100 \times \frac{63}{49} \times \frac{p}{p'}, \text{ or } 128{\cdot}57 \times \frac{p}{p'}.$$

The alkaline liquor is first verified in the manner described for testing the normal sulphuric acid. Suppose that the experiment gives 50. On the other hand, 50 grammes of the nitric acid to be analysed are weighed out, and sufficient water is added to increase the bulk to 500 cubic centimetres. The analysis is made in the same way as for commercial sulphuric acid. If, for ex-

ample, the number of divisions on the burette expressing the quantity of alkaline liquor, is 22, we find :—

$$T = 128{\cdot}57 \times \frac{22}{50} = 56{\cdot}6.$$

Thus 100 kilogrammes of this acid contains 56·5 kilogrammes of monohydrated nitric acid.

This determination may be verified by the density, which, according to the following table of Thénard, gives the real quantity of acid in 100 parts.

Density.	Real acid in 100 parts.
1·513	85·7
1·498	84·2
1·470	72·9
1·434	62·9
1·422	61·9
1·376	51·9

2. *By the oxidation of Proto-salts of Iron.*—A proto-salt of iron heated with nitric acid, is converted into a sesqui-salt, every 6 equivalents of iron thus further oxidized corresponding to 1 equivalent of nitric acid decomposed—

$$NO^5 + 6FeO = NO^2 + 3Fe^2O^3.$$

This method, as first proposed by Gossart, and afterwards modified by Pelouze and by Fresenius, is fully described in the chapter on Saltpetre (pp. 331—334).

*Schloesing's Method.**—This method, like that of Pelouze, is founded on the reducing action of boiling hydrochloric acid and protochloride of iron on nitrates:

$$NO^5 + 6FeCl + 3HCl = NO^2 + 3Fe^2Cl^3 + 3HO.$$

The binoxide of nitrogen evolved in the reaction, is collected over milk of lime, to free it from any hydrochloric acid that may pass over with it, and carefully preserved from contact of air, then transferred into another vessel, and converted into nitric acid by mixing it with oxygen in a vessel containing water; and the quantity of this acid is determined volumetrically by means of a standard solution of lime in sugar-water. This method has the advantage of not being affected by the presence of organic matter —which would vitiate the result obtained by Pelouze's process, by reducing a portion of the permanganic acid used to oxidize the

* Chem. Gaz. 1854, p. 398.

proto-salt of iron (p. 332), and make the amount of nitric acid come out too small. It has been applied by Schloesing to the determination of nitric acid in tobacco; but it is difficult of execution, and not generally applicable.

3. *By the reducing action of Mercury* (Crum's method).*—This method resembles the last, inasmuch as it depends on the collection of the binoxide of nitrogen evolved in the reaction; but differs from it, in completing the determination by the direct measurement of this gas, instead of by its reconversion into nitric acid. A weighed quantity of the nitrate is introduced into a graduated glass tube filled with mercury and standing over mercury; a quantity of water sufficient to dissolve the salt is then passed up, and lastly a large excess of strong sulphuric acid. The nitric acid thus set free is reduced by the mercury to binoxide of nitrogen, which collects at the top of the vessel, the decomposition, accelerated by occasional agitation, being complete in about two hours. The level of the sulphuric acid is then read off, and a warm concentrated solution of protosulphate of iron is passed up to the top of the liquid. This absorbs the whole of the binoxide of nitrogen, leaving only a small quantity of nitrogen, arising from air left in the tube. The volume of gas absorbed is then observed, and the amount of nitric acid in the salt thence determined by calculation. This method, which gives exact results, has been applied by Crum to the determination of nitric acid, not only in saltpetre, but also in gun-cotton, after he had ascertained that the presence of organic matter did not interfere with the liberation of the binoxide. To introduce the gun-cotton, and likewise pulverulent substances, above the mercury, Crum encloses them in a small glass tube. H. Rose recommends wrapping them in filtering paper.

4. *By the reducing action of Copper at a red heat.*—Nitric acid and all other oxides of nitrogen are completely deoxidized by red-hot copper. The nitrogen is liberated as gas, and may be collected and measured over mercury. The apparatus used is exactly similar to that employed for the absolute determination of nitrogen in organic bodies. At the closed end of an ordinary combustion tube is placed a quantity of bicarbonate of soda, capable of yielding, by ignition, sufficient carbonic acid gas to sweep all the air out of the tube; beyond this is placed the

* Ann. Ch. Pharm. lxii, 233.

nitrate to be analysed, and the remainder of the tube is filled with copper turnings or finely-divided copper, reduced by hydrogen; the combustion-tube is connected by a gas-delivery tube with a graduated jar filled with acid standing over mercury, and a quantity of strong potash-solution is passed up to the top of the jar, to absorb the carbonic acid evolved. Heat is then applied, first to the bicarbonate of soda, till the air of the tube has been completely expelled by the carbonic acid evolved; the metallic copper at the other end is next heated to redness; and then heat is applied to the part of the tube containing the nitrate. The nitric acid thereby evolved is reduced to free nitrogen by the copper, and passes over into the receiver. When the decomposition is complete, heat is again applied to the bicarbonate of soda, to sweep out all the nitrogen remaining in the apparatus, and drive it into the graduated jar, the carbonic acid which passes over at the same time being absorbed by the potash. The gas in the jar is then left to cool; its volume read off, due corrections being made for pressure and temperature; and its weight then determined: 1 part by weight of nitrogen corresponds to 3·857 parts NO^5.

If the nitrate contains water, a chloride-of-calcium-tube must be inserted between the combustion-tube and the gas-delivery tube, in order to absorb the water, and determine its amount by weight.

5. By conversion into Ammonia.—Nitric acid, as already observed (p. 355), is converted, by the action of nascent hydrogen evolved by the action of zinc on dilute acids or on solution of potash, into ammonia, each equivalent of ammonia produced corresponding to 1 equivalent of nitric acid,

$$NO^5 + 8H = NH^3 + 5HO.$$

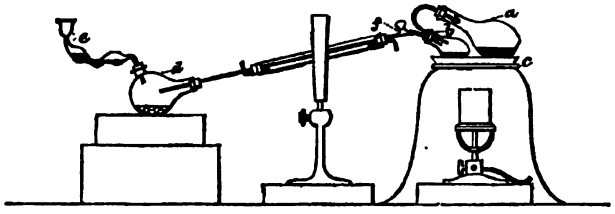
The reaction may be applied in various ways to the estimation of nitric acid.

a. Martin's method.—The salt or solution containing the nitric acid (after being boiled with excess of potash, to expel any ammonia that may be present,) is treated with washed metallic zinc and sulphuric or hydrochloric acid; and, after the reaction is finished, the liquid is distilled with potash, to expel the ammonia, which is either estimated volumetrically by means of a standard acid liquid, or received in a bulb-apparatus containing hydrochloric acid, and subsequently precipitated by bichloride of platinum. A considerable quantity of zinc must be used, equal to

at least four times the weight of the nitric acid to be estimated because a portion of the hydrogen always escapes in the free state without acting on the nitric acid. The reaction is not interfered with by the presence of nitrogenous organic bodies, such as uric acid, quinine, the organic matters in mineral waters, &c.; gelatin retards it, but does not interfere with the final result.

*b. Harcourt's method.**—In this process, the hydrogen is evolved by the action of caustic potash-solution on zinc in contact with iron (p. 355). The apparatus used consists of a generating flask, *a* (Fig. 157), having a capacity of 200 cubic centimetres.

FIG. 157.



This is connected by a bent tube, drawn out and curved at its extremity, with the smaller flask or bulb, *b*, and the two are so arranged that they both rest at a considerable angle of inclination on the sand-bath, *c*. The smaller flask, *b*, is connected with a condenser leading into a small tubulated receiver, *d*. In the upper part of the condensing tube is a small tubulure, closed during the distillation by a caoutchouc plug. The tube *e*, which is provided with two or more bulbs and a funnel-head, is fastened into the tubulure of the receiver *d*, by a perforated caoutchouc plug, which, when slightly greased, makes a tight and supple joint. A standard solution of sulphuric acid is used for the collection and determination of the ammonia, the excess of acid employed being finally determined by means of a standard solution of caustic potash.

The following is the course of the operation:—The funnel *e* is brought into the vertical position by being turned round in the tubulure through half a circle; and a quantity of standard acid from a burette is passed through it into the receiver, more than sufficient to neutralize all the ammonia that can be formed. Some

* Chem. Soc. J., xv, 383.

litmus solution is added, to render visible the progress of the action. The funnel-tube is then restored to the horizontal position, and its bulbs filled, up to the proper level, with the standard acid; the total quantity of acid taken, is read off from the burette, and the flask *a* is removed, its tube and cork, together with the smaller flask, which should contain a little water, remaining in position on the sand-bath. Fifty grammes of finely granulated zinc is introduced into it, together with half that quantity of iron filings, which have been cleansed by sifting, and ignition in a covered crucible; a weighed portion of the nitrate to be determined is then introduced, together with sufficient water to dissolve it; and, lastly, a measured quantity of a solution of caustic potash, free from nitrate, and the flask immediately replaced. It is essential that the quantity of the metals and of the potash employed, should greatly exceed that which is theoretically necessary for the complete conversion of the nitric acid. In operating upon nitrate of potash, 0·5 grammes of that substance, 20 cubic centimetres of water, and 20 cubic centimetres of a solution of potash of specific gravity 1·3, are found to be good proportions. Provided the quantity of potash be sufficient, the degree of dilution is immaterial, since, in the course of the distillation, it passes through every stage of concentration. It must not be highly concentrated at the beginning of the operation.

Heat is now applied to the part of the sand-bath immediately beneath the larger flask, and the liquid is gradually raised to the boiling-point. If the bubbles of air and hydrogen pass through the bulb-tube *e*, at a moderate rate, there is no risk of loss of ammonia. When distillation has commenced, the lamp is so placed, that the water in the flask *b*, may also gently boil. The liquid is thus twice distilled in one operation, and the traces of potash which escape from the flask *a*, are effectually retained in the flask *b*. For further security, the end of each of the two exit-tubes, is drawn out and bent into a hook. Repeated experiment has proved the efficacy of this arrangement for keeping back, in a slow distillation, everything that is not volatile. The quantity of liquid in the flask *b*, can be regulated by adjusting the position of the lamp. The distillation, which should occupy from one to two hours, requires only occasional attention. It may be terminated when hydrogen gas, which is evolved in larger quantity as the potash becomes concentrated, has been passing regularly for five or ten minutes through the bulb-tube *e*. When the fluid in *e*

has receded, as the apparatus cools, into the inner bulb, the caoutchouc plug is withdrawn from *f*, and a stream of water poured into the condensing tube, to preclude the possibility of ammonia being retained upon any portion of its surface. The tube *e* is then turned round into the vertical position, and water is passed through it two or three times, after which it is removed, and the tubulure of the receiver is closed by a cork. Finally, the receiver itself is disconnected; the end of the condensing tube is rinsed externally, and the determination is completed by adding a standard alkali from a burette to the liquid in the receiver, till a change of colour appears. Collection in hydrochloric acid and precipitation by chloride of platinum may be substituted, but the volumetric method gives perfectly good results.

The zinc and iron which remain in the generating flask, need only be washed with water, with dilute acid, and again with water, to be ready for a second determination. Metals which have once been used, generate hydrogen far less actively than zinc with a bright surface and freshly ignited iron; but the production of ammonia proceeds as readily with the one as with the other.

It might be safely assumed that the presence of any salts which are without action upon potash, zinc, or iron, would not interfere with the reaction upon which this method depends; and experiment has shown that the result is not affected by the presence of sulphate of potash or chloride of sodium.

For the estimation of nitric acid in other than alkaline nitrates, it is sometimes advisable to separate the base before proceeding to determine the nitric acid as above. Nitrate of baryta, when directly submitted to this method of analysis, gives perfectly good results; but nitrate of lead showed a slight deficiency in the amount of nitric acid, due probably to an action of dissolved oxide of lead on the surface of the zinc.

6. *By reduction to Binoxide of Nitrogen, and subsequent conversion of that compound into Ammonia* (Ville's method).* —The conversion of the nitric acid into binoxide of nitrogen is effected, as in Pelouze's method (p. 365), by boiling the solution of the nitrate with protochloride of iron and free hydrochloric acid; and the binoxide is converted into ammonia, either by passing it, mixed with hydrogen, over platinum-sponge heated nearly to redness,—

$$NO^3 + 5H = NH^3 + 2HO,$$

* Compt. rend. xli, 939 and 987.

by which method, however, the conversion into ammonia is completely effected only when the quantity of binoxide present is very small, that is to say, when only a small quantity of nitrate is operated on; or, secondly, and more effectually, by passing the binoxide of nitrogen, mixed with hydrosulphuric acid gas, over nearly red-hot soda-lime,—

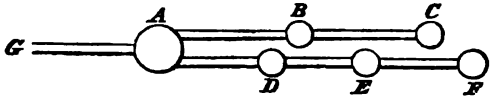
$$NO^2 + 3HS + 2CaO = NH^3 + CaO.SO^3 + CaS^2.$$

In either case, each equivalent of ammonia produced, corresponds to 1 equivalent of binoxide of nitrogen, and therefore also (p. 365) to 1 equivalent of nitric acid.

The ammonia produced by the reaction is collected in an absorption-apparatus in a measured quantity of standard sulphuric acid, and the excess of acid used, is determined by a standard alkaline solution.

The arrangement of the apparatus may be understood from the annexed diagram (Fig. 158). The flask D contains a solution of

FIG. 158.



protochloride of iron with excess of hydrochloric acid, to which liquid the solution of the nitrate to be analysed is added. This flask communicates on one side with an apparatus, F, for generating hydrogen, this gas, before passing into the flask, being washed in the bottle E,—and on the other side with a flask A, which is connected with the tube G, containing soda-lime, and also with the sulphuretted hydrogen apparatus C, through the medium of the wash-bottle B. The tubes proceeding from B and D are made to dip under mercury in A, in order to regulate the flow of the gases. The apparatus having been put together and made air-tight, hydrogen is evolved for eight or ten minutes, to expel the atmospheric air, after which the soda-lime is heated, the evolution of sulphuretted hydrogen commenced, and when the apparatus is well filled with that gas, the liquid in the flask D is quickly heated to boiling. Binoxide of nitrogen is then evolved, and after about ten minutes' slow boiling, is completely converted into ammonia and carried away. The evolution of hydrogen is continued during the whole time of the ebullition. A few lumps

of chloride of calcium are placed in the flask A, to retain any water that may be carried over into it.

This process was especially devised for the estimation of small quantities of nitric acid existing in plants, soils, waters, &c. From 10 to 100 grammes of the substance (or of the residue obtained by evaporating a water) is exhausted with boiling water, and the concentrated solution treated as above described.

GUNPOWDER.

French, *Poudre à tirer, Poudre à canon;* Italian, *Polvere da cannone;* Spanish and Portuguese, *Polvora;* German, *Schiesspulver;* Dutch, *Bulkrind;* Danish, *Krodt, Pulver;* Swedish, *Krut;* Russian, *Porock;* Polish, *Proch;* Turkish, *Barout.*

Few inventions have exercised so prominent an influence on civilization as that of gunpowder; its introduction completely changed the art of war, and so far modified the institutions and forms of government, as to constitute a great epoch in the history of the world. Popular tradition has ascribed it, in Germany to Berthold Schwartz, a Benedictine monk, who lived about the beginning of the fourteenth century, and in this country to Roger Bacon, about the middle of the thirteenth; but recent investigations have traced it back to a much earlier date, and shown that, in all probability, it originated in India or in China.

The Chinese, under the Emperor Koung Ming, 200 years before Christ, are said to have been acquainted with various incendiary compounds, known as *fire of heaven, earth-thunder, devouring fire,* &c., the invention of which, according to Chinese historians, was of much more ancient date. Allowing for some exaggeration in this claim of high antiquity, it appears certain that the simpler effects of gunpowder, such as fire-works, the projection of rockets, &c., were known to the Chinese in the earlier centuries of the Christian era; and Uffano, an Italian historian, affirms that, not only gunpowder, but ordnance, were used in China in the year 85, and that, in his day, cannon, both of iron and of brass, were remaining from very ancient times, in some of the maritime provinces of that empire.

In India, the use of incendiary compounds more or less resembling gunpowder, may be traced to at least as early a date as in China, if not earlier. In the code of Hindoo laws, indeed, the invention of these inflammable compositions is referred to a date which Oriental antiquarians have regarded as coincident with the time of Moses. A more definite statement is to be found in the life of Apollonius Thyanæus by Philostratus, the purport of which is, that Alexander, in his expedition into India, was deterred from attacking the Oxydracæ, a tribe dwelling between the Hyphasis and the Ganges, because they were under the care of the gods, and overthrew their enemies with thunder and lightning, which they shot from their walls. That incendiary compositions, more or less resembling gunpowder, should have been invented in India at a very early date, is not surprising, when we take into account the abundant occurrence of saltpetre as a natural production in that country.

From the East, the art of making incendiary projectiles appears to have been carried to Western Asia and to Europe. The celebrated *Greek fire*, which was first used at Constantinople about the end of the 7th century, and at a later date caused so much terror to the Crusaders, against whom it was employed by the Saracens, was probably derived by the Romans from the Chinese, with whom, in the early centuries of the Christian era, they had frequent commercial relations, the Chinese then carrying on an active commerce on the borders of the Red Sea. It is remarkable, indeed, that the term "Greek fire" is used only by European writers, whereas the Arabian author, Hassan Abraman, who wrote a treatise on pyrotechny, in the ninth or tenth century, designates the projectiles charged with this inflammable mixture, as *Chinese wheels, flowers, lances*, or *arrows;* terms which plainly indicate its Eastern origin.

The composition of Greek fire was for a long time kept secret, and the most terrible penalties were threatened against any one who should divulge it; but the engines which served for projecting the Greek fire, described in the "Tactics" of Leo VI., and by other writers of the same date, bear so close a resemblance to those employed for similar purposes by the Chinese, and afterwards by the Arabians, that it is scarcely possible to avoid ascribing to them a common origin. Moreover, the manuscript work entitled *Liber ignium ad comburendos hostes*, attributed to Marcus Græcus, who wrote in the ninth or tenth century, con-

tains about thirty recipes for the preparation of incendiary compounds used by the Greeks, the composition of which also tends to confirm this common origin. The construction of the rocket, and the composition of the mixture for charging it, are described in this work with the greatest exactness, and show that this mixture was essentially the same as gunpowder. The author even recommends the charcoal of willow-wood, which modern experience has shown to be one of the best that can be used as an ingredient of gunpowder.

Gunpowder is mentioned for the first time by one of the names by which it is at present known, in an Arabic treatise on the art of war, by an author who lived in Egypt about the year 1249. The following is a literal translation of the passage into French by M. Reinaud, "La poudre (*El Baroud*) rampe en scorpions; ceux-ci s'allument, s'enflamment, et éclatent là où ils sont poussés; ils s'étendent comme un nuage; ils mugissent comme si c'était le tonnerre; ils s'embrasent comme un incendie et reduisent tout en cendres." This description of a projectile charged with powder agrees in all essential particulars with that of the Greek fire by the Byzantine writers.*

* Greek fire is, however, described by most writers as a liquid compound possessing the property of spontaneous inflammability on coming in contact with the air. Gibbon, in the tenth volume of his "Decline and Fall," after cautioning his readers against too implicit a reliance on the Byzantine writers, says, "From their obscure and perhaps fallacious hints, it would seem that the principal ingredient of the Greek fire was the naphtha or liquid bitumen, a light, tenacious and inflammable oil, which springs from the earth and catches fire as soon as it comes in contact with the air. The naphtha was mingled, I know not by what method, or in what proportions, with sulphur and with the pitch that is extracted from evergreen firs. From this mixture, which produced a thick smoke and a loud explosion, proceeded a fierce and obstinate flame, which not only rose in perpendicular ascent, but likewise burnt with equal vehemence in descent or lateral progress; instead of being extinguished, it was nourished and quickened by the element of water; and sand, urine, or vinegar were the only remedies that could damp the fury of this powerful agent, which was justly denominated by the Greeks, the liquid or maritime fire. For the annoyance of the enemy, it was employed with equal effect by sea and land, in battles and sieges. It was either poured from the rampart in large boilers, or launched in red-hot balls of stone and iron, or darted on arrows and javelins twisted round with flax and tow, which had deeply imbibed the inflammable oil; sometimes it was deposited in fire-ships, the instruments of a more ample revenge, and it was commonly blown through tubes of copper, which were planted in the prow of a ship, and fancifully shaped into the mouths

From Egypt, the use of gunpowder gradually extended over the countries which were brought under the Mohammedan rule, that is to say, the countries on the coast of Africa, whence it soon passed into Spain, where we read of its employment at the siege of Niebla, in 1257. It is also mentioned in an Arabic poem on warlike engines, the author of which lived in 1272. The date at which the use of igneous projectiles began to extend in Western Europe, is not exactly known; but whether the Crusaders ultimately became acquainted with the Arabian processes, or the capture of Constantinople, in 1204, led to the discovery of the secret of the

of savage monsters, that seemed to vomit a liquid and consuming fire." A similar account of the modes of projecting the Greek fire is given by Beckman; and the Princess Anna Comnena says, it was composed of sulphur, resin, and oil. (See Popular Science Review, No. 10, January, 1864.)

It is scarcely necessary to observe, however, that liquids like naphtha or bitumen, either alone or mixed with sulphur, are not spontaneously inflammable, though they may burn very fiercely when once set on fire. The slow spontaneous ignition of masses of tow or other fibrous material saturated with oil, is altogether beside the question. Neither could such a liquid possess any *explosive* force, even when burnt. The Greek fire, if of such a nature as these writers describe, could only have been projected by mechanical means, and if so, it is difficult to understand how it could have been set on fire. For these reasons it is most probable, as stated in the text, that the real explosive and igniting power resided in a composition of the nature of gunpowder, that is, a composition containing a body, like nitre, capable of supplying the oxygen required to burn the inflammable materials. It is by no means impossible that rockets may have been used, loaded with flax or tow impregnated with an inflammable liquid, and projected by the force of gunpowder. The historian Joinville (*Histoire de St. Louis*), quoted by Gibbon, speaking of the Greek fire, says: "It came flying through the air like a wing-tailed dragon, about the thickness of an hog's head, with the report of thunder and the velocity of lightning; and the darkness of the air was dispelled by this deadly illumination."

With regard to the modern "Greek fire" used at the siege of Charleston, we can have no difficulty in believing the assertion made respecting its liquidity and spontaneous inflammability, inasmuch as modern chemistry is acquainted with numerous liquids possessing this power. Sulphide of phosphorus, and solutions of phosphorus alone, or of phosphorus and sulphur in volatile liquids, such as bisulphide of carbon, possess all the properties ascribed to the spontaneously inflammable Greek fire. Specimens of Greek fire which have reached this country from America are of two kinds: a liquid consisting simply of rectified mineral oil or petroleum,—and a solid quite similar to rocket composition, rammed into small iron tubes, which are fired at the enemy, enclosed in shells, and are ignited and scattered by the bursting of the shells. From the accounts received of the effects of these compositions, neither of them appears to be very destructive.

Greek fire, it is certain that the works of Albertus Magnus, and, as already mentioned, those of Roger Bacon, contain descriptions of compositions apparently extracted from the work of Marcus Græcus. Roger Bacon, indeed, intimates that the use of explosive mixtures among the nations of Western Europe was restricted rather by religious scruples than by ignorance of the methods of preparing and using them. These scruples, however, gradually disappeared; for in the chronicles of Froissart, we find mention of the Greek fire, or of similar compositions, which bear a striking resemblance to those described by Marcus Græcus. These facts show that the secret of the Greek fire was not lost, but that, on the contrary, the use of it extended in the West, that it merely changed its name in course of time, and that the employment of this mixture in its original form was ultimately superseded by that of more effective compositions.

Rockets, known in Europe by the name of Greek fire, appear to have been used by Western as well as by Eastern nations long before the invention of guns. But towards the end of the fifteenth century, when fire-arms were so far improved as to admit of taking a tolerably exact aim, the rocket fell into disuse in European warfare, and continued to be employed only by nations amongst whom the art of war was less advanced. It was, however, used by the Hindoos with great skill against the English in the wars of Tippoo Saib, and was thence re-introduced into Europe by some British officers who had observed its efficacy, and is now, after many improvements, established in use as the Congreve rocket.

That which for a long time prevented the Chinese, Arabians, and Greeks from using gunpowder as a means of propelling balls, was probably the impurity of the saltpetre which they used, and perhaps also the imperfect manner in which the materials of their powder were mixed, whence it would naturally result that the proportions of charcoal, sulphur, and nitre which now yield a detonating compound, would in their hands have produced only a deflagrating substance. The first mention of a cannon in European warfare, is by an Arabian author, who speaks of it as employed in 1323, by the King of Granada, at the siege of Baza. An authentic record of the republic of Florence, dated February the 11th, 1325, shows that fire-arms were known in Florence at that date. Italian historians speak of their use in 1326, and of the services which they rendered in the attack of

Cividale in 1331. The use of these arms soon extended to France, as may be seen from the accounts of expenditure in that country from 1335 to 1345. The first use of cannon in France was at the siege of Puy-Guillem in 1339; and in 1345, twenty-four cannons were cast, and sixty pounds of powder made at Cahors. Field artillery is said to have been first used by the English at the battle of Cressy, in 1346.

The use of powder for springing mines under fortresses, was first tried about the middle of the fourteenth century, but it was not till many years afterwards that this mode of attack was so far improved as to be really effective.

The peculiar action of Gunpowder.—That gunpowder is a mixture of saltpetre, sulphur, and charcoal, and that its action on ignition, is dependent upon the instantaneous evolution of a large quantity of heated gas, which communicates a sudden, powerful shock to everything in its vicinity, is well known to everybody. But the reason why not one of the similar substances, exerting still greater power, of which chemistry can produce so many, is capable of replacing gunpowder, is worthy of more minute investigation. Several of these substances, like the chloride of nitrogen, explode with such slight force, that they cannot be handled without the greatest danger. The same is the case with the material used for lucifer-matches, and with detonating powder. Independently of this, there are several other important circumstances to be taken into consideration. Imagine the ball in a gun-barrel, at the moment of ignition, when it is forced forward by a sudden impulse; it is evident that a certain, although hardly appreciable, space of time is necessary to overcome the inertia of the ball. An open door can easily be shut by the little finger, time being allowed for this slight force to overcome the inertia of the door, whilst bullets from a gun will pierce it, but have no power to move it. The same is the case in the barrel of a gun. When the velocity of the explosion does not allow time for the gases to communicate their motion to the ball, it remains nearly immovable, and becomes, as it were, one of the sides of the barrel, which must then burst like a bomb. Fulminating silver, and fulminating mercury, are, for this reason, useless as powder; the application of chlorate of potash, instead of saltpetre, in powder, also renders its action too rapid, and is attended with danger in the preparation. An experiment, in-

stituted with that substance by Berthollet, at the powder mill of Essonne, cost two workmen their lives. The most explosive of all substances, is the chloride of nitrogen; a drop in an open saucer makes a hole in the bottom of the vessel and in the support, because all its particles are decomposed at the same instant. Gunpowder, on the contrary, burns with a certain degree of tardiness, so that the time during which the combustion is proceeding, can be observed and measured. In addition to this, powder has the incalculable advantage, that all its ingredients are cheap products, and that the manufacture may be carried on in any country.

Products of Decomposition.—The quantity and composition of the gases evolved in the combustion of gunpowder, depend upon the proportions in which the nitre, sulphur, and charcoal are mixed. The view regarding the decomposition of powder hitherto adopted, and still very generally believed to represent approximately the principal changes which occur, supposes that the whole of the nitrogen in the powder is set free, and that the whole of the oxygen of the nitre enters into combustion with the charcoal, forming carbonic acid, carbonic oxide, or a mixture of the two, while the potassium of the nitre combines with the sulphur, forming protosulphide of potassium.

1. If the whole of the carbon is converted into carbonic acid, the decomposition must, on the above hypothesis, be supposed to take place as shown by the equation—

$$KNO^6 + S + C^3 = KS + N + 3CO^2,$$

and the powder will contain

1 equivalent of nitre	101	74·9
1 „ sulphur	16	11·8
3 „ carbon	18	13·3
	135	100·0

yielding by combustion—

3 equivalents of carbonic acid . .	66	48·9
1 „ nitrogen	14	10·4
1 „ sulphide of potassium . . .	55	40·7
	135	100·0

Consequently, 1 volume of the powder should yield—

Nitrogen . . .	93 parts by weight	=	74·6	volumes of gas.
Carbonic acid. .	440 „ „	=	221·4	„
Total. . . .			296·0	„

2. If the carbon is wholly converted into carbonic oxide, the decomposition will be

$$KNO^6 + S + C^6 = KS + N + 6CO,$$

and the powder must contain

1 equivalent of nitre	101	65·4
1 „ sulphur	16	10·4
6 „ carbon	36	24·2
	153	100·0

yielding by combustion :—

6 equivalents of carbonic oxide . .	84	54·9
1 „ nitrogen	14	9·1
1 „ sulphide of potassium	55	36·0
	153	100·0

Consequently 1 volume of the powder should yield,—

Nitrogen . . .	83 parts by weight	=	66 volumes of gas.
Carbonic oxide .	439 „	„	391	„	„
Total			457	„	„

It appears, then, that the second kind of powder is capable of yielding 1⅛ times as great a volume of gas at the same pressure and temperature as the first; but, on the other hand, carbon, in burning to carbonic acid, evolves a far greater quantity of heat than in burning only to carbonic oxide, and the greater expansion of the gases thence resulting, more than compensates for the smaller quantity of gas originally produced. Moreover, the second kind of powder burns so slowly, that the combustion is not complete by the time the ball issues from the gun, so that part of the projectile force is lost. Experience has shown that the best kinds of powder, for fire-arms, both large and small, are composed very nearly in the proportions indicated by the first of the formulæ above given, as may be seen by comparing the percentage composition of the various kinds of powder for fire-arms, given in the following table, for which we are indebted to the kindness of Professor Abel, with the theoretical composition of the powder No. 1.

In all these kinds of powder, the proportions of the ingredients are nearly the same, the variations arising chiefly from the different degrees of purity of the materials used; in some, the proportion of charcoal is increased, and that of sulphur diminished, to allow for the smaller percentage of carbon in the charcoal em-

Analyses of English and Foreign Gunpowders.

	Nitre.	Sulphur.	Carbon.	Water.
English.				
Waltham Abbey, L. G.*	74·6	10·0	14·8	0·8
Pigou and Wilks, L. G.	77·0	7·6	14·7	0·7
Hall and Son, L. G.....	74·6	10·5	14·1	0·8
Curtis and Harvey, L. G.	75·4	10·1	13·7	0·8
Waltham Abbey, F. G.	74·8	9·7	14·9	0·6
Foreign.				
French, L. G.	74·0	12·6	12·5	0·9
Belgian, L. G.	75·7	10·0	13·5	0·8
American, L. G.	74·4	9·7	14·9	1·0
Prussian, L. G.	76·6	10·0	12·8	0·6
Do. F. G.	75·5	11·0	12·8	0·7
Austrian Rifle	75·4	9·1	14·7	0·8
Swedish, L. G.....	74·9	9·7	14·6	0·8
Russian, F. G.	74·4	9·4	15·7	0·5
Swiss Rifle, Globular	71·1	10·3	17·8	0·8
Chinese, L. G.	71·4	11·3	15·7	1·6

* L. G., large grain; F. G., fine grain.

ployed; in others, the percentage of nitre is somewhat increased, probably to obtain a more rapidly burning powder.

Blasting powder usually contains a larger proportion of sulphur, which is a cheaper material than charcoal, and may be used in excess in the composition of this powder, but, if present in large quantity in powder for fire-arms, would corrode the metal. The composition of French blasting powder, and of its products of combustion, is approximately that which is indicated by the equation:

$$KNO^6 + S^2 + C^4 = KS^2 + N + 2CO^2 + 2CO.$$

100 parts of this powder contain 64·3 parts nitre, 20·4 sulphur, and 14·7 charcoal, and should yield by combustion 39·0 parts by weight of KS, 9·9 N, 31·2 CO^2, and 19·9 CO.

The actual products of the combustion of gunpowder are, however, at least under certain circumstances, more complicated than the preceding theory would indicate, the residue of the combustion being found to contain sulphate and carbonate of potash, as well as sulphide of potassium. When powder burns in contact with the air, a great portion of the sulphide of potassium formed in the first instance, is converted into sulphate by oxygen derived from the air; and this secondary combustion is, partly at least, the cause of the flash which issues from the muzzle of a gun at the moment of discharge; but the sulphate and other oxygen-salts of potash

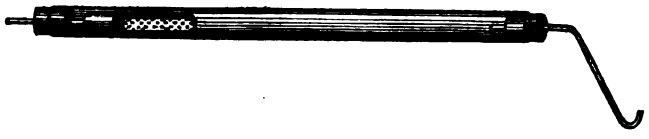
are likewise found in the residue—sometimes, indeed, constituting the greater part of it—even when the powder is burned in close vessels or in a vacuum; under such circumstances they must evidently be regarded as direct products of the combustion of the powder.

Gay-Lussac and Chevreul, by burning gunpowder in a copper tube, obtained a gaseous mixture containing, in 100 parts, 45·4 parts CO^2, 37·5 N, 8·1 NO^4, 0·6 carburetted hydrogen, and 8·3 of a peculiar gas containing carbon, hydrogen, and oxygen. In another experiment, they obtained 53 per cent. CO^2, 42 N, and 5 CO. The solid residue was found to contain sulphate, carbonate, and the higher sulphides of potassium, as well as the protosulphide.

More elaborate investigations of the products of combustion of gunpowder in close vessels have been made of late years by A. Vogel, jun. (Dingl. pol. J. cxxxvi, 156), by Bunsen and Schischkoff (Pogg. Ann. cii., 321; Wagner's Jahresb. 1857, p. 131; 1858, p. 158); by Linck (Ann. Ch. Pharm. cix., 53); and by Karolyi (Phil. Mag. [4] xxvi., 272). The experiments of Bunsen and Schischkoff were made with sporting powder; those of Linck with Wurtemburg war-powder; and those of Karolyi with Austrian war-powder.

The apparatus used by Bunsen and Schischkoff for the qualitative examination of the products of combustion of gunpowder, consists of a wide glass tube, *d*, fitted with a cork, *b*, through which is inserted, air-tight, a brass tube 250 millimetres

FIG. 159.



long, 2 millimetres wide, and closed at the end, *a*. The finely pulverized gunpowder is tightly pressed into this brass tube, and as soon as it has been set on fire, and burns with a steady hissing flame from the mouth of the brass tube, this tube is fitted air-tight, by the cork *b*, into the glass tube *d*,—a perforated tin tube or thin glass tube, *c*, being, however, interposed, to protect the

tube *d* from the immediate contact of the flame, which would probably break it. The solid residue remains in the brass tube *a*; the smoke of the burnt powder collects in the tube *d*, while the gaseous products of the combustion make their escape by the bent tube *e*, and may be collected over mercury in a state of purity, provided the air in the apparatus has previously been thoroughly expelled by these gases.

The solid residue and the smoke of the powder, were found to consist of *sulphate, hyposulphite, carbonate, hydrate,* and *nitrate of potash; sulphide* and *sulphocyanide of potassium; carbonate of ammonia, sulphur,* and *charcoal;* and the gaseous products, of *nitrogen, carbonic acid, carbonic oxide, hydrogen, hydrosulphuric acid,* and sometimes considerable quantities of *nitric oxide,* and even *nitrous oxide.*

For the quantitative estimation, the powder was made to fall in a very fine stream into a glass bulb heated to redness by a lamp, whereby it was burnt continuously, and without explosion. The solid residue remained in the bulb, while the smoke and gaseous products of the combustion were drawn by an aspirator, first through a long straight glass tube in which the smoke condensed, then into a series of small glass tubes, connected by narrow necks. These tubes, when filled with the gases, were sealed and separated by directing the blowpipe flame on the narrow necks, and the gases were thus preserved for analysis.

The powder used by Bunsen and Schischkoff, in their experiments, had the following composition:—

Nitre		78·99
Sulphur		9·84
Charcoal	Carbon	7·69
	Hydrogen	0·41
	Oxygen	3·07
	Ash	trace
		100·00

The fixed residue of the combustion was found to have very nearly the same composition as the smoke, and the two together gave, by analysis, the following composition of the solid products of the combustion.

Sulphate of potash	62·10
Carbonate „	18·58
Hyposulphite „	4·80
Sulphide of potassium	3·13
Sulphocyanide „	0·45
Nitre	5·47
Charcoal	1·07
Sulphur	0·20
Sesquicarbonate of ammonia	4·20
	100·00

The gaseous products contained in 100 volumes:—

Carbonic acid	52·67
Nitrogen	41·12
Carbonic oxide	3·88
Hydrogen	1·21
Hydrosulphuric acid	0·60
Oxygen	0·52
	100·00

1 gramme of the powder was found to yield, by combustion, 0·680 grammes of solid products (fixed residue and smoke) and 0·314 grammes of gases. Hence, and from the percentage composition of these products above given, the complete decomposition of the kind of powder examined by Bunsen and Schischkoff, may be represented by the following scheme:—

1 grm. of powder consisting of

	Grm.
Nitre	0·789
Sulphur	0·098
Charcoal: C	0·076
Charcoal: H	0·004
Charcoal: O	0·030

yields by combustion

		Grm.
Residue, 0·680	$KO \cdot SO^3$	0·423
	$KO \cdot CO^2$	0·126
	$KO \cdot S^2O^2$	0·033
	KS	0·021
	KC^2NS^2	0·003
	$KO \cdot NO^5$	0·037
	C	0·007
	S	0·001
	$2NH^4O \cdot 3CO^2$	0·029
		0·680

Gases, 0·314	Grm.	Cub. cent.
N	0·0998	= 79·40
CO^2	0·2012	= 101·71
CO	0·0094	= 7·49
H	0·0002	= 2·34
HS	0·0018	= 1·16
O	0·0014	= 1·00
	0·3138	= 193·10

Linck (Ann. Ch. Pharm. cix, 52) has examined, by the method above described, the products of combustion of the Wurtemburg war-powder (p. 380); and Karolyi has investigated those of the war-powder (for small arms and ordnance) of Austria. His results, though obtained by a different method, approach more nearly than those of Linck, to the results which Bunsen and Schischkoff obtained with sporting powder.

Karolyi's method consisted in exploding the gunpowder in a vessel capable of offering a certain resistance, and placed within a 60 pound mortar which is capable of being exhausted, the powder being then exploded by the galvanic method.

FIG. 160.

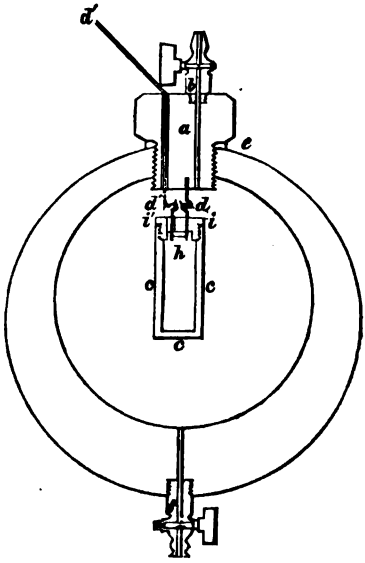


Fig. 160 represents a section of the apparatus: *a*, is a strong iron nut screwed into the touch-hole of the mortar, and provided with a good stuffer, so that the mortar can be made air-tight. The screw is provided at *b* with a short tube closed by a cock, by which the vacuum is obtained in the subsequent operations. At *d'* a copper wire, well insulated by gutta-percha, passes through the nut, while at *d* is a small hook; to this and to the insulated copper wire, the vessels filled with gunpowder are fixed, so as to admit of the ignition of the charge. The explosion vessels consist of cast-iron cylinders closed at one end, while at the other is a nut, through which the arrangement for a galvanic explosion passes. For this purpose, the nut is provided with an excavation in which a thin platinum wire is fastened on the one hand to the insulated copper wire, and on the other to the copper wire which passes directly through the nut. Outside the cover, the wires are bent into knots, which, as previously mentioned, serve to support the cylinder and complete the voltaic circuit.

To make an experiment, the mortar is exhausted; the tap closed; and the platinum wire in the charge ignited by the cur-

rent from six Smee's elements, and thus the vessel is burst. It is readily seen that in this way it is possible not only to burn the gunpowder under different resistances, but also to obtain the resultant gases free from atmospheric air. The resistance of the explosion vessels must be so chosen, that the gas in the mortar, after explosion, has an excess of pressure of half an atmosphere inside, that it may be subsequently transferred to the measuring vessels.

The following table exhibits the composition of the several kinds of powder used in the experiments above mentioned, together with the composition of their several products of combustion.

I. Composition of Powder.

	Bunsen and Schischkoff.	Linck.	Karolyi.	
	Sporting Powder.	War Powder.	Small-arm Powder.	Ordnance Powder.
Nitre	78·99	74·66	77·15	73·78
Sulphur	9·84	12·49	8·63	12·80
Charcoal: Carbon	7·69	12·31	11·78	10·88
Charcoal: Hydrogen	0·41	0·54	0·42	0·38
Charcoal: Oxygen	3·07		1·79	1·82
Ash	...	..	0·28	0·31
	100·00	100·00	100·05	99·97

II. Gaseous Products of Combustion, by Volume.

	Bunsen and Schischkoff.	Linck.	Karolyi.	
	Sporting Powder.	War Powder.	Small-arm Powder.	Ordnance Powder.
Nitrogen	41·12	34·68	35·33	37·58
Carbonic acid	52·67	52·14	48·90	42·74
Carbonic oxide	3·88	4·33	5·18	10·19
Hydrogen	1·21	1·63	6·90	5·93
Hydrosulphuric acid	0·60	7·18	0·67	0·86
Oxygen	0·52	0·04	...	...
Marsh gas	...	...	3·02	2·70
	100·00	100·00	100·00	100·00

III. Total Products of Combustion, by Weight.

	Bunsen and Schischkoff.	Linck.	Karolyi.	
	Sporting Powder.	War Powder.	Small-arm Powder.	Ordnance Powder.
Sulphate of potash	42·27	29·01	36·17	36·95
Carbonate „	12·64	15·43	20·78	19·40
Hyposulphite „	3·27	9·63	1·77	2·85
Sulphide of potassium	2·13	3·75	...	0·11
Sulpho-cyanide „	0·30	1·16	...	...
Nitrate of potash	3·72	1·20	...	...
Charcoal	0·73	1·84	2·60	2·57
Sulphur	0·14	0·31	1·16	4·69
Sesqui-carbonate of ammonia	2·86	2·05	2·66	2·68
Nitrogen	9·98	9·55	10·06	9·77
Carbonic acid	20·12	22·47	21·79	17·39
Carbonic oxide	0·94	1·18	1·47	2·64
Hydrogen	0·02	0·03	0·14	0·11
Hydrosulphuric acid	0·18	2·38	0·23	0·27
Oxygen	0·14	0·01	...	...
Marsh gas	...	...	0·49	0·40
Loss	0·56	...	0·68	0·17
	100·00	100·00	100·00	100·00
Quantity of gas (in cubic centimetres) for 1 grm. of powder.	192·10	218·35	226·59	200·90

A comparison of these results, shows that the composition of the powder has a great influence on the nature of the products of the combustion: for in Bunsen and Schischkoff's powder, which contains much nitre, nearly 4 per cent. of this substance is found in the residue, while, on the other hand, in the residue of the ordnance powder, which contains less nitre, almost 7 per cent. of sulphur and charcoal are separated unburnt. When the reducing body preponderates, the combustion of the powder is comparatively imperfect. The gases from sporting powder, in which the nitre is in large proportion, contain only 3 per cent. of carbonic oxide; whereas the gas from the Austrian ordnance powder contains nearly 10 per cent. The quantity of hydrogen and of marsh gas increases in the same direction, so that the products of combustion of the ordnance powder contain nearly 20 per cent. of combustible gases. These gases, in fact, like those proceeding from the combustion of gun-cotton, may be ignited by a glowing piece of wood.

The preceding results are completely at variance with the

older theory, which supposes that powder is resolved by combustion into carbonic acid, nitrogen, and sulphide of potassium: for, in the first place, whether the combustion takes place in contact with air, as in Bunsen and Schischkoff's experiments, or in a vacuum, as in those of Karolyi, the fixed residue contains but a very small quantity of sulphide of potassium; and, secondly, according to the equation on page 378, the volume of the carbonic acid should be, to that of the nitrogen, in the ratio of 3 to 1; whereas in Linck's experiments, this ratio is only 1½ to 1, and in all the others, considerably less.

The approximation of the best kinds of powder to the composition indicated by the equation just quoted, is, however, too great to be regarded as merely accidental. Moreover, the peculiar mode of combustion adopted in the experiments just quoted may have given rise to a considerable difference between the products of combustion thus obtained, and those which are formed in ordinary cases; in fact, when a gun is discharged in the ordinary way, the residue of the combustion is found to contain a considerable quantity of sulphide of potassium. Further investigation is therefore required before we can determine with certainty what will be the products of combustion of a particular powder under given circumstances, and what will be the best proportion of the ingredients for obtaining from a given bulk of powder the greatest possible quantity of gas at the highest temperature.

The results obtained by Bunsen and Schischkoff as to the temperature of the flame of gunpowder, and the mechanical effect of its explosion, will be considered in subsequent pages.

MATERIALS OF GUNPOWDER.

1. *The Saltpetre.*

Crude saltpetre cannot be used in the manufacture of gunpowder. The crystalline flour, quite free from chloride (p. 304), is the best material for the purpose. In France, the amount of chloride is not allowed to exceed $\frac{1}{1000}$. At the Waltham Abbey mills, the washing process is carried so far, that nitrate of silver produces no precipitate in a solution of the purified saltpetre. If the pure saltpetre-flour is to be stored, it is spread out in shallow pans, after having been thoroughly drained; and these are exposed for some hours to a temperature of about 180° to 200° F., in a capacious and well-ventilated drying chamber. But,

for general use in the manufacture of gunpowder, the drying operation is dispensed with; the moisture contained in the well-drained saltpetre-flour is determined, and an allowance is made for it in weighing the proportion of saltpetre, which is then mixed, in its damp condition, with the other ingredients. Thus the employment of the saltpetre-flour saves two preliminary operations in the manufacture of gunpowder, namely the drying, and the grinding of the saltpetre before mixture with the charcoal and sulphur. The dampness of the saltpetre prevents loss from dusting in the mixing process.

2. *The Sulphur.*

The sulphur is used either in the form of *flowers*, obtained by passing the vapour into a condensing chamber, where it collects on the walls in the form of fine powder, or in that of rolled sulphur, obtained by pouring the melted sulphur into cylindrical moulds (see SULPHUR, Vol. I, Part III, p. 7). At Waltham Abbey the roll and rock sulphur of commerce are purified by distillation, a small proportion of flowers of sulphur being produced at the commencement of each operation, which is employed only for pyrotechnic purposes. The main product of the purification is crystallized rock sulphur, which is ground very finely before it is mixed with the charcoal and saltpetre. Continental manufacturers also generally prefer the rolled sulphur, although it requires mechanical pulverization, because it is less apt to contain gritty particles, and is free from sulphurous acid, which the flowers often contain, in consequence of the inflammation of the sulphur at the commencement of the distillation, when the retort and condensing chamber still contain atmospheric air. The sulphur may, however, be obtained free from sulphurous acid, by allowing it to condense upon damp cloths; or it may be freed from the acid, by leaving it between the damp cloths for a short time before use.

3. *The Charcoal.*

The influence which the *charcoal*, by reason of its porosity, inflammability, &c., exerts upon the quality of the powder, is very considerable. The quality of the charcoal, again, depends upon the material from which it is prepared, and upon the method of its preparation. Proust's experiments have thrown considerable light upon the former of these points. He found that a mixture of 72 grains of saltpetre was consumed with:

12 grains of carbon from	In seconds	Leaving a residue of
Hemp stalks	10	12 grains.
King's spear	10	12 „
Vine-branches	12	20 „
Chick-pea stalks	13	21 „
Pine-wood	17	30 „
Berry-bearing alder (*Rhamnus frangula*)	20	41 „
Spindle-tree (*Euonymus europæus*)	21	27 „
Hazel	23	30 „
Horse-chestnut wood	26	36 „
Walnut	29	33 „
Coke	50	45 „
Sugar	70	48 „

whilst carbon from rice, starch, albumen, blood, leather, &c., would produce no detonation. It is obvious from this table, that the soft, woody parts of plants produce the best charcoal; nitrogenized animal matters produce the worst. For the same reason, paper is not applicable, in consequence of the size it contains, whereas the fibre of flax and old linen is an excellent material for the purpose. In Spain, the preference is given to hemp charcoal. Whatever kind of wood is employed, those parts must be thrown aside which carbonize in the manner of starch or albumen, &c. For this reason, the bark, which is impregnated with gummy, mucilaginous and extractive matters, besides salts, must be peeled off from the wood for charring, all the leaves and smaller branches removed, and wood which is not too old, and yet fully developed, should be selected. Branches from 1 to 2 inches in thickness, yield the best charcoal. It is also found advantageous to expose the peeled boughs to the rain for some time, which removes still more of the extractive matter.

Charcoal for making gunpowder is usually prepared by heating wood in iron cylindrical retorts, the volatile products of the distillation being either condensed and utilized for the preparation of acetic acid, &c. (Vol. I, Part I, p. 340), or conducted by pipes into the fire, and there consumed.

The preparation of charcoal in cylinders requires the most accurate regulation of the heat throughout the whole operation. Furnaces are used for this purpose, with cylinders walled into

them (Figs. 161 and 162), somewhat resembling the coal-gas fur-

FIG. 161.

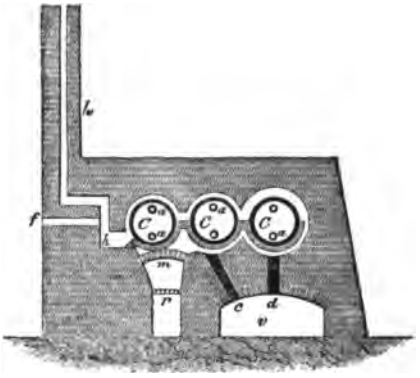
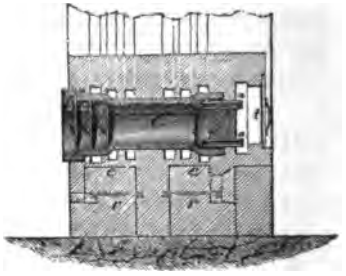


FIG. 162.



naces. The three cylinders, *C C C*, are of cast-iron; the front part projects out of the furnace, and can be closed air-tight by the three doors *o o o*. The hinder part is let into the back of the furnace, so that the wall both supports and closes it. The pipes *a a* which are seen walled in at this part, and connect the cylinder with the space *t* immediately before it, are intended, partly for the reception of the test-woods, and partly for conducting the gases and vapours through walled channels to a separate cistern. The flame-fire, which is made upon the grates *r*, *r*, is more uniformly disseminated by the pierced arch *m*; it first surrounds the lower halves of three cylinders, and then the upper ones, by the flues *e*, *e*, *e*, and finally escapes by the chimney *h*. At *f* there is a damper. When too much ash has collected, it can easily be cleared away through the channels *c* and *d*, which at other times are kept closed. The wood for charring fills the middle, narrow portion of the retorts, the larger pieces being placed on the outside, and the smaller in the interior, having been previously cut to the proper lengths. That the regulation of the process may not be impeded, and a uniform quality of charcoal obtained, it is not advisable to place more than three retorts in one furnace, and these are made only just large enough to hold 100 lbs. of wood; the charcoal is, therefore, rendered somewhat expensive. When all the crevices are luted, the fire is lighted. The progress of carbonization is estimated by the colour of the escaping vapours, and by the appearance of the test-woods, which are frequently

broken lengthways, in order to see whether the decomposition has progressed uniformly from end to end. In about five hours the distillation is in full progress. When the vapours cease to escape, the lids *o o o*, are quickly removed; and the charcoal is allowed to cool in well-closed vessels of cast-iron. It is not found advantageous to quench it in water, as, if it is to be used immediately, which is always desirable, a calculation must be made for the amount of water, or the proportions in the mixture will not be accurate.

Instead of charging the retorts directly with the wood to be charred, it is frequently packed in sheet-iron cases (*slips*) provided with lids, and of such dimensions as to fit easily into the retort. A great saving of time and heat is thus effected, as the charges can be withdrawn and renewed, without allowing the fire to go down.

When the slips containing the finished charcoal are withdrawn from the retorts, their contents are at once transferred to iron cylinders, provided with lids, in which the charcoal cools out of contact with air.

One circumstance which always occurs during charring, requires particular notice. In the cooler parts of the distilling apparatus, tar is constantly condensed, and is decomposed on dropping back upon the hot charcoal, leaving a difficultly combustible coal as residue. This and the half-charred portions, must be carefully removed. They amount sometimes to 5 per cent.; but, in furnaces of the best construction, this quantity is reduced to ½ per cent.

The degree of carbonization of wood depends upon the temperature to which it is subjected. A full red heat yields charcoal containing about 90 per cent. of carbon, and 7 to 8 per cent. of hydrogen-compounds. Such charcoal, when properly prepared from well-selected woods, has a bluish-black appearance and a velvety lustre when powdered: it should be light, sonorous, firm, and slightly flexible. This "black charcoal" is exclusively used in England for the manufacture of gunpowder.

If, on the contrary, the wood be heated only to a temperature approaching redness (about 282° C. or 540° F.), a charcoal is obtained called "red charcoal" (*Charbon roux; Rothkohle*), containing from 70 to 72 per cent. of carbon, and 28 to 30 per cent. of hydrogen and oxygen. This degree of carbonization is attained in the distillation process above described, by extinguish-

ing the fire when the escaping vapours appear yellow, and the test-woods are brittle and present a yellowish-brown shining fracture, the heat of the furnace being then sufficient to complete the carbonization. The charcoal thus obtained should be brown, with veins of a lighter colour, smooth, with a number of cross fissures, but none lengthways; when pounded, it should have the appearance of black shot velvet; it should burn with a bluish flame, and dissolve almost entirely in caustic potash.

This red charcoal appears to contain the maximum amount of inflammable matter of the wood: it is therefore more economical than black charcoal when used as fuel; it also burns with greater facility, because it possesses less power of conducting heat, and, consequently, the heat communicated to one part of it, is less easily taken away.

The higher inflammability of the red charcoal causes gunpowder made with it to burn with greater energy than that prepared with black charcoal; but, on the other hand, the red charcoal contains about 28 per cent. of hydrogen and oxygen in the proportion to form water (which consequently add nothing to the combustion), and only about 2 per cent. of hydrogen above this amount, while the proportion of carbon contained in it is also comparatively small: hence a larger proportion of it must be used to produce the required decomposition; and the powder prepared with it is less dense, and more liable to dust and absorb moisture. The large quantity of aqueous vapour, formed from the oxygen and hydrogen present in the proportion to form water, will moreover absorb a considerable quantity of the heat generated by the combustion, and thereby diminish the expansion of the gases, upon which, as already observed, the propelling force mainly depends: the expansion of the steam itself will, however, add something to the effect produced.

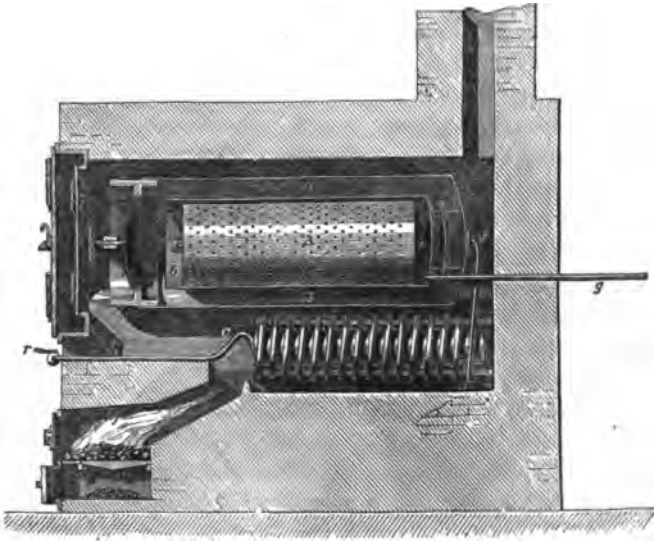
For the reasons just stated, black charcoal is preferred for the manufacture of powder by all English manufacturers. In France, Belgium, and most parts of the Continent, red charcoal is preferred for sporting powder, on account of the higher inflammability of the powder which it yields, but black charcoal is universally employed for war-powder.

In preparing red charcoal by the ordinary method of carbonization in cylinders, already described, very great care is required in regulating the temperature, as, if it rises too high, black charcoal is obtained instead of red.

To ensure the application of a due degree of heat and the speedy removal of the gaseous products of the distillation, M. Violette has invented a method of *Carbonization by superheated steam*. This process is adopted at the powder works of Esquerdes, near Saint-Omer, of Saint-Chamas, near Marseilles, and at Welteren, in Belgium.

The apparatus used at Esquerdes consists of three concentric iron cylinders, the innermost of which, A (Fig. 163), pierced

FIG. 163.



with holes all over its circumference, receives the charge of wood. Below these cylinders is a spiral iron tube, *c c*, one end, *d*, of which communicates with a steam-boiler, and the other end, *e*, with the bottom of the outer cylinder, *a a*. A fire, *f*, fed with wood or coke, heats the spiral tube to the required temperature. The cylinder, *a a*, is closed by a wrought-iron plate, and the apparatus is closed by two doors of the same metal, so as to prevent external cooling. A copper tube, *g*, is inserted into the bottom of the interior cylinder, A, for the escape of the steam and the products of the distillation. The whole apparatus is imbedded in solid masonry, close to the building containing the boiler which heats the drying-house.

The fire having been lighted, and the spiral tube heated to

300° C., the cock *r* is opened, to admit the steam, which then rushes through the spiral, where it is heated, into the large exterior cylinder, *a a*, and finds its way into the inner cylinder, A, which is open in front; there it gradually penetrates into the pores of the wood, chars it, and finally escapes by the pipe *g*, carrying with it all the gaseous and tarry products of the distillation. To ensure the complete removal of these products, the steam must have a pressure of at least half an atmosphere above that of the external air; and an excess of a whole atmosphere is still better. The charcoal obtained is then of very fine quality, of black, red, or burnt colour (*brûlot*), according to the heat of the steam and the time during which the wood is exposed to its action, and is quite free from glaze on the surface. If, on the other hand, the steam is at a lower pressure, say one-fourth of an atmosphere, above that of the air, the tarry matters are not effectually swept out, and the charcoal has a glazed surface, arising from a layer of solidified tar, which stamps it as of inferior quality (*charbon verni*), and fit only for the preparation of the coarser kinds of powder, such as blasting powder.

The boiler-furnace is fed with coal; the fire which heats the worm-tube, with coke. The cylinder is charged with 25 to 30 kilogrammes of black alder wood.

The operation lasts from an hour and a half to two hours. Six charges are worked off in a day, yielding altogether about 50 kilogrammes of good charcoal. The quantity of steam required per hour, is 20 kilogrammes at a pressure of one-fourth of an atmosphere, 25 kilogrammes at half an atmosphere, and 45 kilogrammes at one atmosphere. The daily consumption of coal is from 80 to 120 kilogrammes, according to the pressure of the steam. The heating of the worm-tube requires, for each operation, from 15 to 20 kilogrammes of fire-wood, or 5 to 6 kilogrammes of coke, amounting to 150 to 200 kilogrammes of wood, or 60 to 80 kilogrammes of coke, for every 100 kilogrammes of charcoal produced.

Numerous experiments on the comparative advantages of carbonization by dry distillation in closed cylinders (p. 390), and by distillation in superheated steam at the same temperature, have shown, that the two processes yield very nearly the same results, both as to the quantity and to the quality of the charcoal obtained. The average yield of charcoal has been found to be 42·72 per cent. of the wood by the steam process, and 42·80 per cent. by dry distillation. With regard to the quality of the

charcoal and its fitness for the preparation of gunpowder, it is found that war-gunpowder and blasting powder possess the same properties, whether they are prepared with the one or the other kind of charcoal; and the quality of sporting powder has been found, by recent experiments,—contrary to the ideas formerly entertained on the subject,—to depend more on the mode of preparing the powder and the degree of carbonization of the charcoal, than on the particular method of carbonization followed.

Other modes of preparation.—In some localities, where wood is abundant, the charring is sometimes effected in furnaces resembling those used in the coking of coal (Vol. I, Part I, pp. 77 to 114). These are constructed with a flat hearth, covered over by a half-cylindrical arch, and with two doors, one at each end. In the beginning, when the wood with which the furnace has been charged is ignited, both doors are left open. When the fire has burnt up sufficiently, one of the doors is closed; the other, from which the wood was ignited, is left open for the escape of the smoke, and in order that the wood may be reached with the rakes, and that those pieces which no longer burn with flame may be pushed to the back part of the furnace. When the flame is nearly extinguished, the second door is also closed, to diminish the glowing heat. The charcoal may then soon be drawn out, and quenched in boxes of sheet iron.

Notwithstanding the saving of time which is effected by the use of these furnaces, they are, nevertheless, not the most profitable, partly on account of the great waste and production of half-charred wood and tar-charcoal, but, chiefly, because no definite amount of carbonization can be attained in them. They yield nothing but black charcoal.

The ordinary mounds (Vol. I, Part I, p. 68) are not well adapted to produce charcoal for the powder mills, as the smallest particles of sand, introduced into the powder-mixture, might strike fire under the machines, and occasion accidents. Yet, from a very ancient period, a kind of pit carbonization has been practised for this purpose.

Charcoal prepared in pits is still occasionally produced at Waltham Abbey, exclusively for pyrotechnic purposes (fuzes, &c.), the pit-charcoal being somewhat more inflammable and quickly burning than cylinder-charcoal. At some Continental works (*e. g.* at the Government Powder-works at Angoulême) pit-charcoal is still prepared for war-powder.

The pits are quadrangular and flat, and lined with bricks, which are placed upright. A pit, 6 feet deep, and 12 feet in diameter, is large enough to char 20 cwts. of wood. The margin of the pit must be firm and even; soft, clay-like sand, which is easily formed into balls, and woollen cloths, must also be at hand ready for use. The wood is bound up in fagots, consisting of some hundreds of pieces, which are arranged with some degree of regularity in two layers, one upon the other, and project about 4 feet out of the pit. By means of a pole, previously inserted crossways, one row of fagots is easily made somewhat higher than the adjoining one; a channel is thus left, which must be open in front, as it serves for the admission of the materials for igniting. Straw and shavings are inserted and ignited, and the whole contents thus set on fire, the mouth of the channel being immediately stopped up with fagots, to avoid the admission of an excess of air. The flame gradually makes way, at last consuming the pole; the channel becomes closed; and the mass of wood sinks together. When the fire is extinguished, the pit is no longer filled by that which remains; the same number of fagots are, therefore, gradually added, as were at first used. The regular stratification being thus destroyed, it becomes necessary, in order to obtain a uniform state of carbonization throughout, to loosen the mass in some parts, and force it together in others. When the flame is everywhere extinguished, the process is finished. The air is then quickly excluded by throwing the wetted woollen cloths upon the even surface of the charcoal. On the top is thrown a layer of sand, which is firmly stamped down. In three or four days the charcoal may be drawn, and must be carefully separated from half-charred pieces, and from earthy particles. As much as 16 or 17 per cent. of charcoal is obtained by this very imperfect process. Neither the form of the pit, nor the use of sand, can be recommended. Sometimes round iron pans with lids are employed, instead of the pits, which afford a similar kind of coal, and a produce of 23 per cent.

The charcoal from the pits, furnaces, and pans, is black charcoal, and is in the form of long, sonorous rods, which must not be contaminated with tar-charcoal. In contradistinction to this, the charcoal from the cylinders is called "*distilled charcoal.*"

It is always advisable to separate any sand or other impurity from the charcoal, before putting it through any further operation: this is usually done by hand; but in France, during the

Revolution, when saving of time was the great object, the powder was thrown with shovels against a current of air, which carried away the dust.

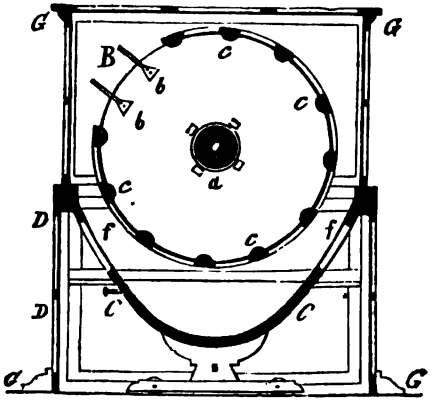
PREPARATION OF THE MIXTURE, AND FURTHER OPERATIONS.

It has already been stated, that the intimate mixture and consequent minute state of division of the particles, are of as much importance to the quality of the powder, as the proper proportion of its ingredients. Hence the great care expended in mixing and pulverizing, and the peculiar arrangement of the apparatus for this purpose. In whatever way it is effected, the object is always the same, namely, to pulverize and mix the constituents into a moist paste, of as great density as possible, which is afterwards separated into grains of equal size. These must be sifted, dried, and sometimes glazed.

The Pulverizing Drums.

These consist of barrels 44 inches long and of about the same diameter, revolving on a common horizontal axis, and having the internal surface fitted with a series of ridges (about twelve), which project about 8 lines. They are sometimes made of wood, but more generally of leather, nailed to a skeleton of wood. A barrel of this kind is shown in Fig. 164: *a* is the axis, *c, c, c,* &c., are the ridges. At *B* there is a flap, or door, which is kept closed by the straps *b b*, and by bolts. To prevent the dust from escaping, the drum is surrounded by a frame of wood *G G G*, which is lined inside with leather. In the lower part of this covering, the side *D D*, is movable, and fastened by bolts, that the trough *C C*, which moves upon rollers, may be moved in and out when the barrel is emptied. To prevent the contents of the barrel from falling at the side, the trough is so shaped that its edge exactly fits the inner funnel-shaped appendage *f f*, of the covering. The pulverization in this machine, is effected by a

FIG. 164.



number of small bronze balls, of the size of marbles (3½ lines in diameter), which are kept in motion by the revolution of the barrel. The velocity must only be sufficient to carry the balls to a certain height, and allow them to fall back over the ridges; too much velocity would cause them to remain firmly pressed against the side, on account of the centrifugal force. For example, in the manufacture of French sporting powder, 36 lbs. of charcoal are placed in the drums with 3 cwts. of bronze balls, and allowed to revolve for twelve hours, at 30 revolutions per minute. At the expiration of this time, the sulphur is added (30 lbs.) in rolls, which is reduced to powder in this manner, and mixed at the same time with the charcoal. On emptying the barrel, the flap is removed, and a sieve of brass placed before the aperture, which is then brought to the lowest position. Thus, the mass only is emptied into the trough, and the balls remain behind.

The saltpetre-flour is added to the mass thus prepared; and that it may be thoroughly mixed, and more finely pulverized, it is made to revolve just as long in another barrel, with tin instead of brass balls.

The bronze balls are liable to wear away in this method of pulverization (an effect partly attributable to the chemical action of the sulphur upon them); they should therefore be cast of as hard a metal as possible (4 copper to 1 tin).

This apparatus was invented in France, during the first Revolution, when it was necessary to prepare large quantities of powder in a short time. The mixture, obtained in the manner just described, was made into a stiff paste with water, then spread 4 inches thick upon a copper plate, and covered with wet linen; upon this was placed a second layer, and so on, for several alternations, and the whole was reduced by a hydraulic press to about ¼th of its original thickness, then dried by exposure to the air, and granulated. The gunpowder thus obtained was of inferior quality; but the process, called the "revolutionary process," was rapid, and satisfied the pressing demands of the time. As a whole, it has for the most part fallen into disuse; but the pulverizing drum is still very generally used by continental manufacturers, for effecting the preliminary mixture of the ingredients, before subjecting them to the action of the stamping mill or edge-stones; and at the Royal Powder-works at Spendau, in Prussia, the gunpowder is made entirely according to this system.

Powder Mills with Stampers.

The old method of pulverizing, mixing, and pressing the mass, which is still in use at the French Government works and at private works in Germany and other parts of the Continent, is that of the stamping mills (Figs. 165—170), in which the three operations are performed at once, and on a large scale, with pestles set in motion by machinery. The mortars *g g* (Fig. 168), are a series of nearly circular hollows, cut in a solid oaken block, in which the pestles move up and down. These pestles are fitted with a bronze shoe, *b*, at the end, into which the rod is fixed, by driving up the wedge *c* and the shoe *b* at the same time. It is well known that wood offers much less resistance in a cross direction to the fibres, than in the same direction with them; in the former position, the fibres easily split away, in the latter they wear out much less rapidly. From the position of the mortar-block, the blows of *b* would naturally fall across the grain; for this reason, a piece of hard wood, *d d*, is inserted at that part. To give greater strength to the block, it is surrounded with strips of metal, *f*, and holdfasts, *e*, *e*, which must all be covered with

FIG. 165.

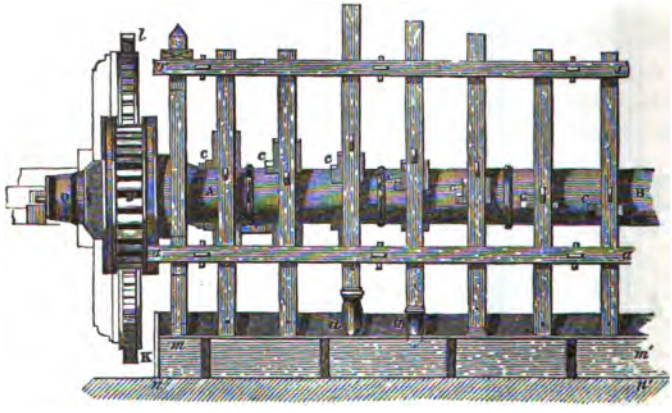
FIG. 166.

FIG. 167.

FIG. 168.

wood, that no sparks may be struck. The form of the stampers, and of the mortar, is by no means a matter of indifference, as the uniform mixture of the ingredients of the paste is mainly dependent upon it. When both parts have the form represented in Figures 165, 166, and 168, the mass is then squeezed by every blow towards the sides, rises higher and higher, until at last it bends over and comes again under the stamper. The mortars are 14 inches in diameter, and 9 inches at the mouth; they are placed 17 or 18 inches apart from centre to centre. A mill has generally two rows, each consisting of ten mortars. Each row is set in motion by a shaft, O A B (Fig. 169), furnished with cams, C. The two parallel shafts fit, by means of a wooden trundle, L, into a wooden cog-wheel, I K, fixed on the driving shaft of the water-wheel which gives motion to the whole machinery. The cam-shafts make four revolutions while the water-wheel makes one; and, as they revolve, the cams catch the cross pieces, *m* (Figs. 165, 167), fixed on the stampers by the wedges *n* (Fig. 165), and thus work the stampers up and down. The cams are arranged on the shafts in a spiral line, so that the same number of stampers is always raised at once, and the charge of the machinery remains constant. The motion of the stampers is guided by two horizontal

FIG. 169.



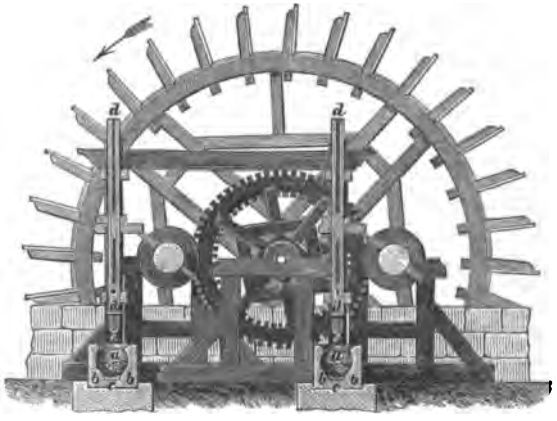
cross-pieces, *u u'*, *v v'*, the lower of which serves also to keep the stampers raised while the charge is being removed from the mortars. For this purpose, a wooden bolt is inserted into the hole *v* (Fig. 166), in the highest position of the stamper, and this

remains supported by the cross beams, so that the cams no longer touch it: each single stamper may thus be put out of gear.

Fig. 170 is a cross section of the mill, showing the manner in which the stampers are raised by the cams. The stampers weigh 80 lbs., one half of which weight is that of the bronze shoe, which is made of an alloy of 100 copper to 22 tin; the other half is the weight of the rod, which is grooved to make it lighter.

In weighing the mixture, it is divided into portions of 20 lbs. each, that being the quantity worked in each mortar. Saltpetre and sulphur are placed in one vessel by themselves, and the charcoal in another. The process begins with the pulverization of the latter. All the mortars are first charged with charcoal, which is thoroughly moistened with somewhat less than an equal quantity of water. The stampers are then set in motion. These are raised twice by each turn of the wheel, and to a height of 1½ feet, giving about sixty blows per minute. The charcoal is reduced to a soft paste in twenty or thirty minutes. The machine is then stopped, the charcoal thrown out upon the sides is carefully scraped back into the mortars, and the saltpetre and sulphur are added with about half as much water as was used before. It is quite impossible, by the mere action of the machine, to obtain a perfectly uniform mixture, because a crust always attaches itself

FIG. 170.



to the bottom of the mortar, which, inasmuch as it no longer follows the course of the other parts of the charge, cannot be

thoroughly powdered or mixed. To ensure a thorough mixture, it is, therefore, necessary to exchange, from time to time, the contents of the mortars with each other. In this operation, all that has attached itself to the sides is carefully scraped out by means of the copper scraper shown in Figure 171, and so much water added as is considered sufficient to retain the doughy consistence of the mass. It is evident that the proper motion of the charge in the mortars must depend upon this state of humidity; if the charge is allowed to be too wet, it will cling with excessive tenacity to the sides of the mortar; and if too dry, it will be easily thrown out. The first exchange is made after 2000 strokes of the stampers, and the following after each 4000. The contents of the first mortar are scraped into a spare vessel, that of the second into the one which has been first cleared, that of the third into the second, and so on, until at length that contained in the spare vessel is emptied into the last. To save time, the first and sixth are emptied in simultaneously. After the last exchange, the stampers are allowed to work without interruption for two hours, to give density to the mass. The whole process in the mortars lasts fourteen hours, during which the mass receives 30,000 strokes, and four hours of this time are occupied in transposing the charges. When the pulverization has been previously effected in the drums, and the mixing and thickening have only to be done by the stamp-mills, the requisite time is, of course, proportionately shortened.

FIG. 171.

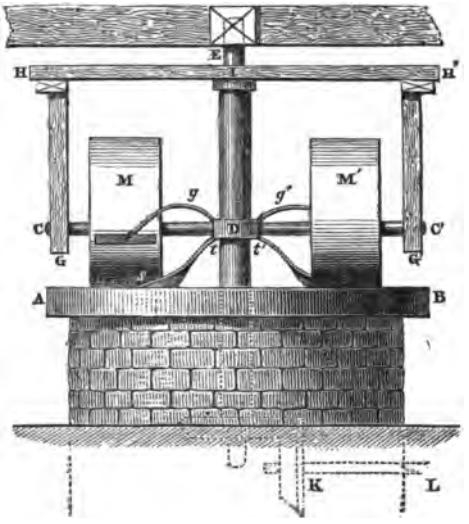
In Italy, heavy metallic mortars are used; in Switzerland, for instance, at Bern, where a celebrated kind of powder is made, hammers moved by water-power are employed, instead of stampers.

Powder-mills with Edge-runners.

This kind of mill, which is the same as that employed for crushing oil-seeds, &c., is invariably used in this country for incorporating, and also partly for pulverizing the ingredients of gunpowder. It is also used on the Continent for the incorporation of the finer kinds of powder, viz., *sporting* powder, after the ingredients have undergone a preliminary mixing and pulverization in the revolving drums already described. It consists of two upright stones or metal runners, M, M′ (Fig. 172), turning upon a common horizontal axis, C C′, which again, together with these two runners, turns upon a vertical axis, E F, placed in the centre of

the round flat bed-stone or iron plate, A B, supported on a bed of masonry. Each half of the horizontal axis, C D C′, is fixed at one end to the vertical shaft, E F, at the other to the wooden frame-work, G H H′ G′, firmly attached to the vertical shaft, E F, which is driven by a horizontal shaft, K L, placed below

FIG. 172.



the floor, and communicating with a water-wheel or steam engine. The edge-runners are hewn from a kind of stink-stone, like the French stone found near Namur, or they are constructed of marble, copper, or, as in England, of cast iron, and, to avoid sparks, enclosed in a ring of bronze. The diameter of these edge-runners is 6 feet and less, up to 10 feet, their weight averaging from 2½ to 5 tons; but they are sometimes above and sometimes below that weight. They revolve from eight to ten times per minute, and carry wooden scrapers, *s*′, behind them, to bring back that part of the mass which has been pushed aside, into the track of the runner. Two copper scrapers, *r*, also rub constantly against the surface of the runners, to detach the matter adhering to them. When one of the edge-runners is brought nearer to the vertical axis by the length of its own thickness, than the other, that part of the mass which is squeezed by the one runner into the interior, will then come exactly into the course of the other. The action of these runners is much more suitable than that produced either

by the mortars or drums, as will be easily understood by considering the kind of motion which they undergo. It is first a rolling motion round the horizontal axis, by which the runner acquires a tendency to roll on in a straight line (with the tangent). This tendency is counteracted by the revolution of the whole round the vertical axis, which every instant forces the runner away from the straight direction, and gives it a circular motion. Hence two actions are produced which obtain simultaneously at every instant: one caused by the rolling motion, which merely crushes the matters, and another by the sliding motion, which tears them to pieces. Mills of this kind, therefore, unite the action of simple rollers with that of grinding mills in which the stones move in a horizontal direction. It must be admitted that the process is more dangerous with mills of this construction; but the powder is never ground in the dry state.

Mr. T. W. Willett has patented* a form of incorporating gunpowder-mill in which the beds rotate about a vertical axis, while the horizontal axis of the edge-runners moves only in a vertical plane, its motion being so determined that it shall not approach within a given distance of the bed of the mill, which is thus secured from all risk of contact with the edge-runners and from the consequent danger of explosion. Further, for the more safe and ready discharge and recharging of the mill, it is so constructed that the mill-man can, at will, raise the axis of the edge-runners yet farther from the mill-bed, and so remove them entirely from contact with the charge. A (Figs. 173, 174) is the revolving bed

FIG. 173.

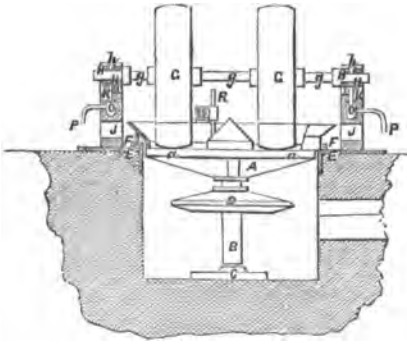
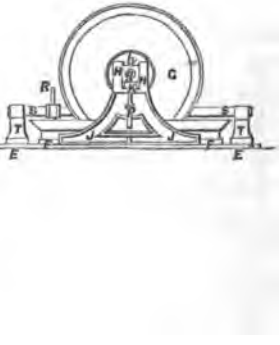


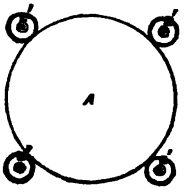
FIG. 174.



* Date of Patent, Dec. 8, 1857, No. 3042.

supported by the vertical shaft B. which revolves in the foot-step C, and is driven by the wheel D. This bed is retained in a horizontal position by four friction-rollers E′ (Fig. 175), attached to the framing E. These friction-rollers take their bearings upon that part of the mill-bed marked *a*. These rollers, and all supporting and driving gearing, are placed below a simple water-joint, F, and are thus protected from the powder. G G are the edge-runners revolving upon the shaft *g g*, which, at its extremities, is fixed by the keys *h h* to two square brass blocks, H H. These blocks have a vertical motion only in the standards J J, and that motion is restricted as to its downward limit by two stops K K, which are so constructed as to allow the edge-runners to approach only within a fixed distance ($\frac{1}{4}$ inch) of the mill-bed, but not to touch it. The advantages of this construction, over the mills commonly employed in this manufacture, are, first, that, as the runners cannot touch the bed, the mill is far less liable to explosions; secondly, that as the edge-runner shafts may all be placed in one line (where several mills are placed near to each other) and the edge-runners themselves, therefore, in parallel planes, an explosion occurring in one mill of the series is far less liable to spread to those adjacent: for the runners themselves will form, to a great extent, a protecting barrier to the force of the explosion also, in the event of an explosion, the risk to the mill-man is greatly lessened, as he can attend to his charge, and yet be, to a great extent, protected by the fixed position of the edge-runners. O O, are two small hydraulic rams, supplied by the pipes P, P, which are connected with the same force-pump; when, therefore, the mill-man requires to remove his charge from the mill, he can, by means of this pump, at once raise the edge-runners from all contact with the charge, when they will cease to revolve; and by the application of a proper wooden scoop to the still revolving mill-bed, the entire charge may be very easily and quickly removed. A fresh charge in like manner can be quickly and easily supplied to the mill-bed, and arranged on it with great evenness and regularity; after this has been done, the edge-runners may be allowed gradually and gently to descend upon the charge. The ploughs R R, in this mill, are held by a plough-beam, S, supported upon the standards T T.

FIG. 175.



In Belgium and Germany, the saltpetre and sulphur are crushed together under the stones, and the charcoal is then added in lumps. At Le Bouchet, in France, where the mill-stones are used principally for sporting powder, the pulverization and the preliminary mixing are generally effected in drums, as described at p. 397, and the thorough incorporation and thickening under edge-stones.

The following description applies to the process as conducted at the Government works at Waltham Abbey, and at the principal English gunpowder manufactories.

The sulphur and charcoal are first ground, the former under mill-stones, the latter in a grinding apparatus similar in construction to an ordinary coffee-grinder. The three ingredients are then weighed out for mixture in the following proportions:

Nitre	37 lbs. 8 oz.
Charcoal	7 „ 8 „
Sulphur	5 „ 0 „
	50 „ 0 „

This constitutes a *charge*, or the quantity of material placed at one time under the incorporating mill.* These quantities are then introduced into the mixing machine, which consists of a wooden box or cylinder, through which there passes an octagonal shaft, provided with a number of fan-like arms. The cylinder is made to revolve round the shaft, which turns at the same time in the opposite direction. From five to ten minutes are allowed for effecting a thorough mixture of the ingredients, after which the powder is removed from the cylinder and filled into bags, which are tied firmly, so as to prevent any separation of the ingredients from each other during their transport to the incorporating mill.

The mixture is then spread upon the bed of the incorporating mill, moistened with distilled water to such an extent as to make the particles adhere firmly, and then submitted to the action of the mill. The runners are not allowed to revolve so rapidly as in the first instance, when the ingredients are merely ground, in order that the particles may be uniformly submitted to the crushing action and pressure of the rollers for a longer time. Towards the end of the operation, they are made to revolve very

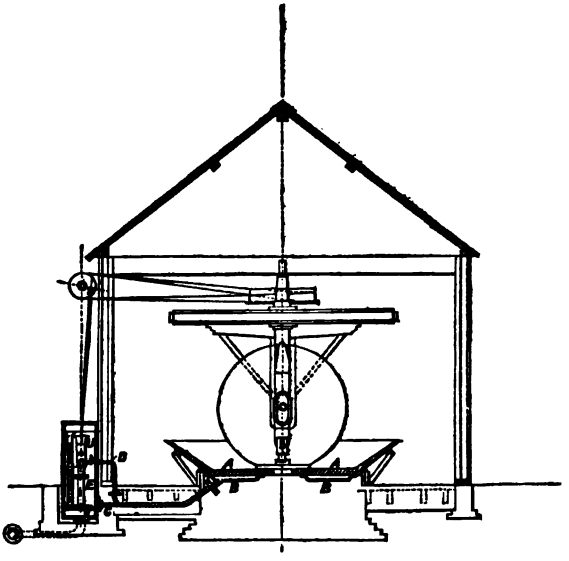
* The charge varies, however, to a certain extent, according to the weight of the runners, those recently made being much heavier than the older ones.

slowly. Great care must be taken that no hard or gritty particles fall on the bed of the mill, and the mass must be kept sufficiently moistened throughout the incorporation, which usually lasts from three to four hours; in the manufacture of Enfield rifle powder, however, the materials are incorporated for five and a half hours.

The process of grinding and combining the materials is sometimes rendered uncertain by variations of temperature and moisture in the external air. To obviate these irregularities, Mr. Edward Hall, of Dartford, has patented* an apparatus for regulating the temperature of the incorporating mills by the application of hot water or other heated liquid, or of steam. When the beds of the mills are of cast iron, the hot water may be introduced directly under them by means of suitable pipes or channels, but when the beds are of marble or other non-conducting substance, and even when they are of metal, the heating by hot water or steam may be applied to the incorporating mill generally, or only in the vicinity of the bed and edge-runners.

Figure 176 shows a transverse section of part of an incorporating gunpowder mill; Fig. 177 is a longitudinal section; Fig. 178 a plan; and Fig. 179 part of an external elevation, with a

FIG. 176.



* Date of Patent, January 11th, 1855, No. 73.

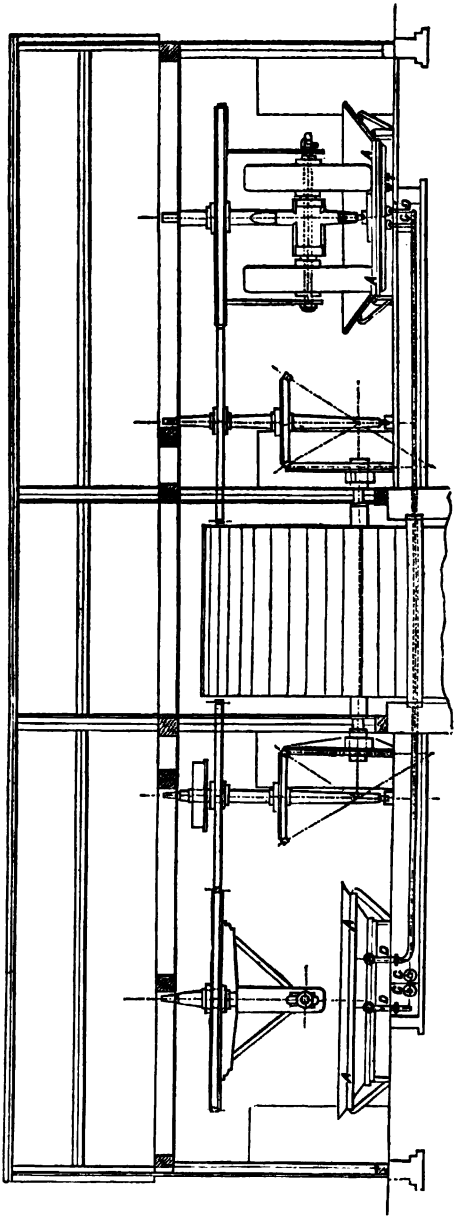


FIG. 177.

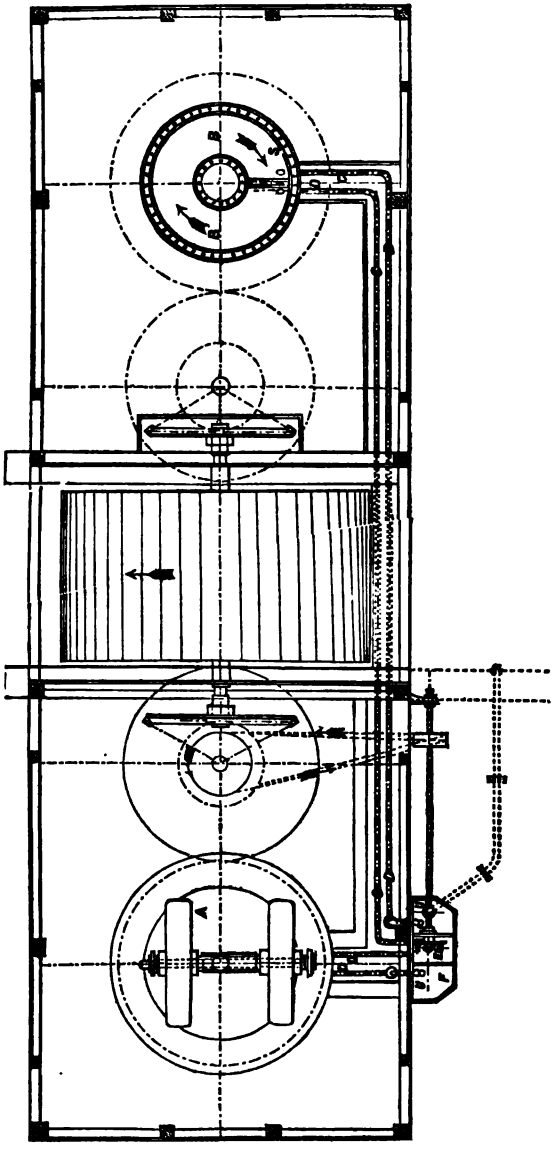


FIG. 178.

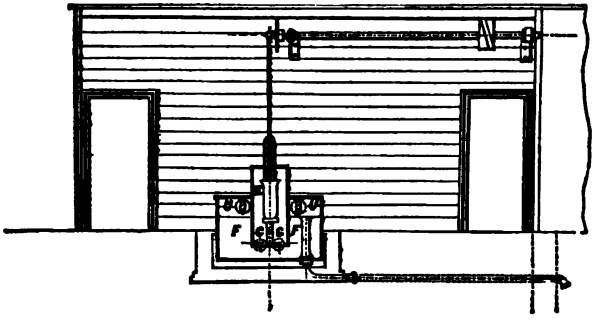
section of the cisterns. These figures represent an apparatus adapted to the circulation of hot water for heating the mills.

The beds, A A, of the mills are here supposed to be of cast-iron; but if marble beds are employed, the most convenient mode of heating is to have the runners partly hollow, and admit the hot liquid into them.

In this arrangement of apparatus, the circulation of the water is most conveniently maintained by the aid of a pump keeping up a constant head of water; but where it can be conveniently so arranged, the apparatus may be constructed for the water to circulate by gravitation only, as is often the case in applying hot water to heat the interiors of other buildings. Under the metal beds, A A, of the mills, are fixed or formed hollow casings or channels, B, through which hot water constantly flows by means of pipes, C and D, from the upper cistern to the casings or channels, B, and back to the lower cistern, F, in the following manner:—

In the upper cistern, E (Fig. 179), the surface of the water is

FIG. 179.



maintained at a greater elevation than in the lower cistern, F, in order to generate a gravitating power sufficient to produce a free circulation of the hot water through the apparatus. Steam is admitted by a pipe into the lower cistern, F, to heat the water contained in it, and the water is raised from the lower into the upper cistern, E, by the pump G, from which it flows through the pipes C to the casing B, and returns by the pipe D to the cistern F. The cocks, U, U (Fig. 178), on the return pipes D, regulate the flow of the hot water through the pipes and apparatus; hence, by the working of the pump, there will be a constant circulation of hot water through the apparatus. It is advisable, for the most

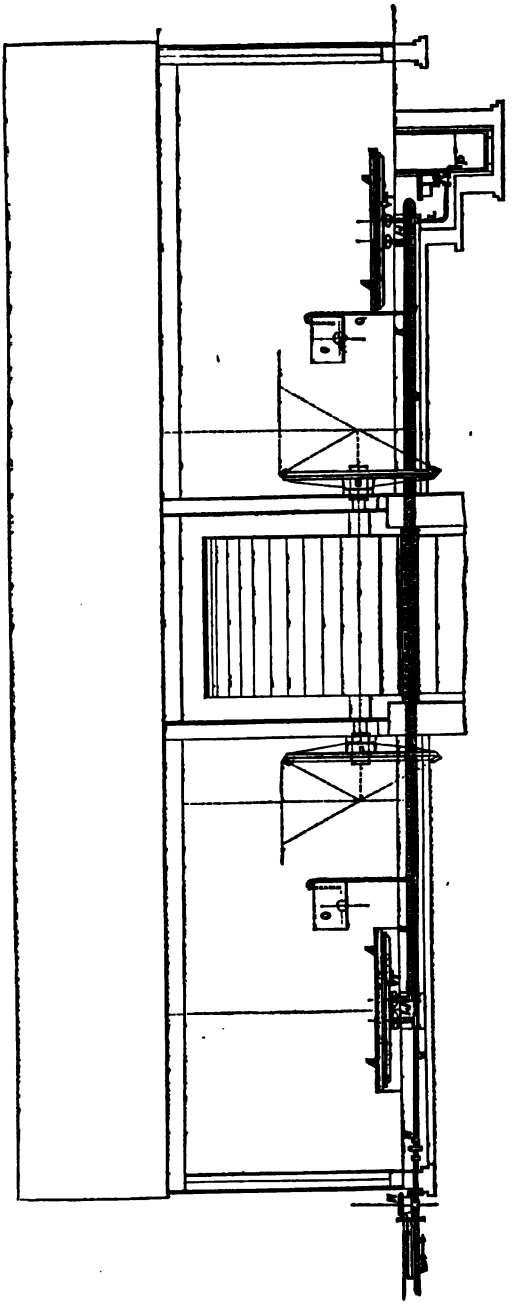


FIG. 180.

part, to keep the water in the upper cistern at a temperature of about 212° Fah., supposing the outer atmosphere to be at about 50°; but in warmer weather the temperature of the water may be proportionably lowered. The temperature of the water may, at all times, be regulated by a cock on the steam-pipe by which steam is supplied to the lower water-cistern, F. The pump may be worked in any convenient manner; in the figure it receives the motion from a crank shaft (on the outside of the building), and is worked by a strap from the water-mill, which drives the edge-runners of the incorporating mills. In order to insure the hot water circulating through the casings or channels, B B, under the mill-beds, there is a partition in each casing or channel between the points where the pipes C and D are connected, so that the hot water coming in at C cannot pass to D without going through the casing or channels B. The ends of the return pipes, D D, are elevated just above the surface of the mill-beds, so that the channels or casings may be kept constantly full of water, and air-pipes, S, with cocks, T, are fitted to them.

Figures 180, 181, and 183 represent a longitudinal section, transverse section, and plan of two incorporating mills, with ap-

FIG. 181.

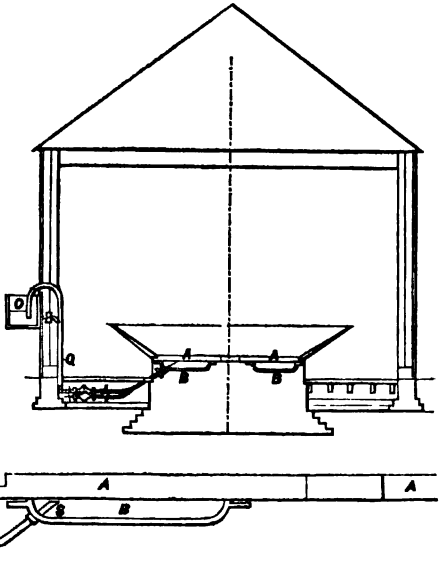


FIG. 182.

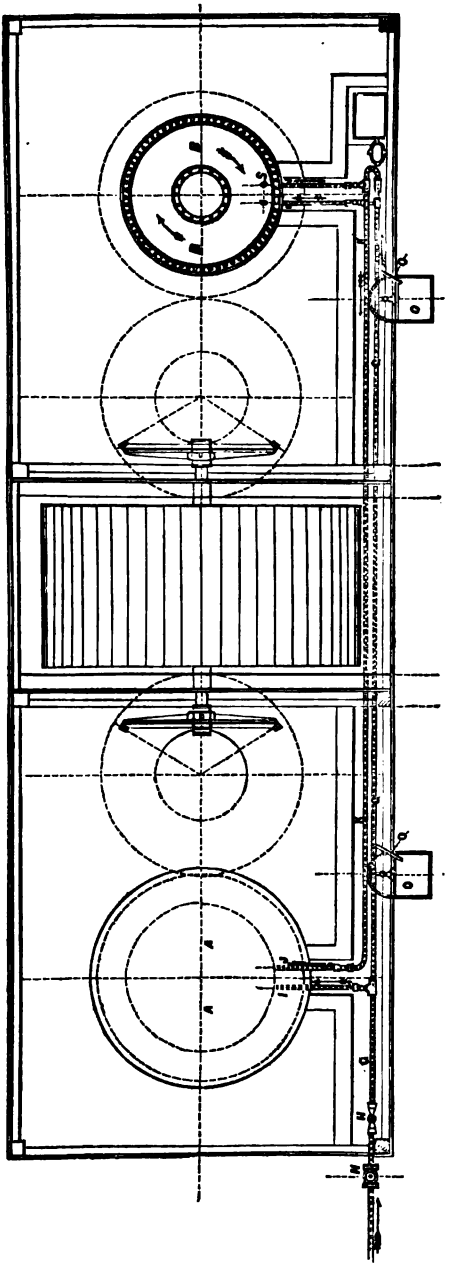


FIG. 183.

paratus arranged for heating by steam. Figures 182, 184, and 185 exhibit some of the parts on a larger scale. G is the steam supply-pipe from a low pressure steam-boiler, the safety-valve of

FIG. 184.

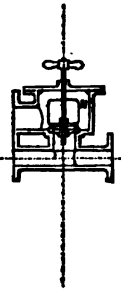
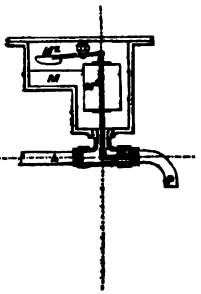


FIG. 185.



which should be weighted at about 1 lb. on the square inch. H is a cock by which the supply of steam may be regulated; H^1 is a safety-valve on the pipe G. The beds, A A, of this mill, as in the previous case, are constructed with hollow casings or channels, B B, into which steam is allowed to flow by means of branch-pipes, I I, on the steam supply-pipe, G; and the condensed steam from the casings or channels, B B, flows through the branches, J J, into the outlet pipe, K, to which the branch-pipe, L, is affixed, and the condensed-water-receiver, M, in which there is a float, M^1 (Figs. 184 and 185), connected with the escape-valve, N, and with the weighted lever, M^2. By this arrangement the apparatus is freed from accumulations of condensed water, which flows from the pipe K, and escapes at the outlet P, when the valve, N, is moved by the rising of the float, M^1. S S, are pipes, having cocks, T T, to allow the air in the casings or channels to escape. In order to have a constant supply of hot water for moistening the ingredients of the charge of gunpowder, cisterns, O O, are fixed outside the building, with cocks passing into the mill, with bent pipes, Q Q, from the steam-pipe, G, which dip into the water contained in those cisterns, to heat it.

Gunpowder incorporating mills, thus heated, should be well ventilated above, in order that the moisture arising from the charge on the beds, may escape freely.

In very hot weather, some gunpowder-makers may desire to cool the metal beds, A, A, of a mill to a temperature of marble beds; this may be done by circulating cold water through the apparatus in place of hot water; Mr. Hall, however, believes it

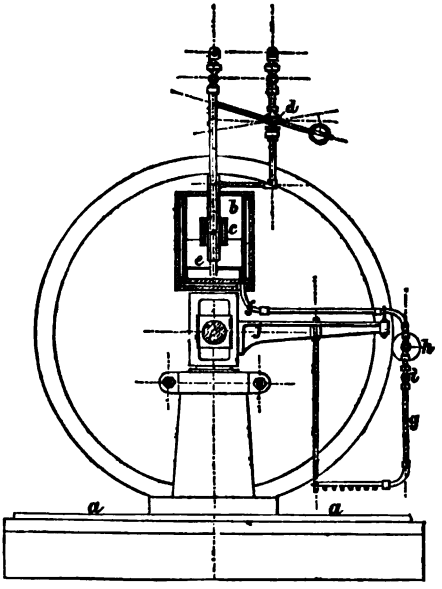
to be highly advantageous, at all times, to heat gunpowder incorporating mills, in such a manner that the gunpowder under process of milling or incorporating, may be heated considerably above the ordinary atmospheric temperature.

For moistening the powder while under the action of the mill, a small watering can, with a very fine rose, is commonly employed; but the moistening thus effected is not always uniform, or limited to the precise quantity required. In the powder-works of Le Bouchet, in France, a funnel, V (Fig. 186), terminating in a horizontal tube, *a*, *b*, pierced with a number of small holes, is fixed behind one of the mill-stones; water is poured into the funnel and discharged at pleasure by opening a cock attached to the vertical tube of the funnel.

FIG. 186.

Still greater regularity in the moistening of the charge is attained by the self-acting apparatus invented and patented by Mr. Hall, of Dartford.* In this apparatus (Fig. 187) a small water-cistern, *b*, is at-

FIG. 187.



* Date of Patent, August 4th, 1855, No. 1773.

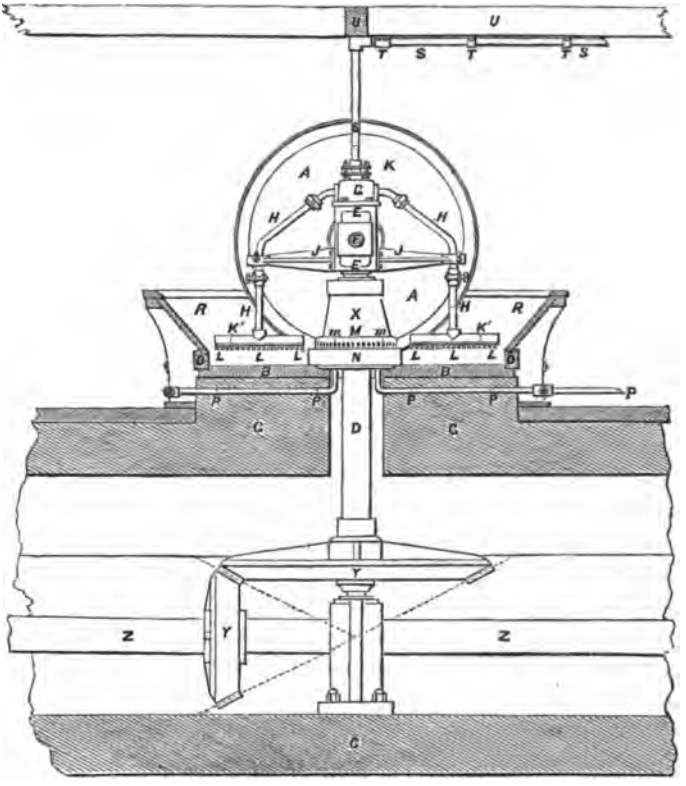
tached to each end of the runner-shafts of the mill, and moves round with the runners. It is supplied with water from a fixed cistern at a higher position. *c* is a float, which regulates the supply by acting on the valve *d*, on the supply pipe. The cistern, *b*, is cased with a jacket when steam is employed for heating the water; *e* is a fine wire strainer; *f* is a pipe or tube by which the water from below the strainer is conducted to the horizontal perforated pipe, *g*, by which it is distributed upon the charge. The quantity of water allowed to flow through the apparatus is regulated by a cock or tap, *h*, which has an index and pointer to show the extent of the opening; *i* is a tap or cock below the cock *h*, for stopping the flow of water; *j* is an arm which carries the distributing apparatus.

Another method of moistening the charge in the incorporating mill, consists in the application of a jet or jets of steam, by which the charge is said to be more regularly and evenly moistened than by jets of water. An apparatus for this purpose, which also comprises an arrangement for subsequently drying the charge by a current of air directed to the interior of the mill, has been patented by Mr. F. W. Willett.* A (Fig. 188) is the runner of the mill; F, the runner-shaft, a portion of which, with one of the runners, is supposed to be removed; S S, is the steam-pipe, attached to the beam U by the clips T T. The steam-pipe, S, passes into the stuffing-box, K, of the small steam-chest, G, which is attached to the head, E, of the driving shaft, D, and therefore revolves with the runners.

From this steam-chest, G, two steam-pipes, H H, pass, which terminate in two other small steam-chests, K^1 K^1, the length of which is about 4 inches less than the width of the mill-bed, and their width from 7 to 8 inches, according to the size of the mill. The bottom of these steam-chests, K^1 K^1, is perforated with small jets or pipes, L L, which are made to rise three-fourths of an inch into the interior of the steam-chests, so as to allow the condensed water to collect in the bottom of the chest, instead of falling upon the charge. I I, are two stop-cocks, by which the amount of steam supplied can be regulated at pleasure. M is an annular pipe, resting upon the central block, N, and connected with the pipes P P. Air from a fanner or other suitable apparatus, is conducted by these pipes, P P, to the annular pipe M, whence

* Date of Patent, June 3rd, 1856, No. 1313.

FIG. 188.



it issues through the small apertures, *m m m*. These apertures should be placed as near the bottom of the annular pipe, M, as possible, so that the current of air issuing from them may be deflected by the central block, N, and compelled to pass above the surface of the charge, in order to ventilate and dry it, and yet not to cause it to rise as dust. This current of air (which may be heated advantageously in damp weather) must be regulated at the discretion of the mill-man, according to the state of the charge; but in all cases the current must be very gentle, and such as not to raise the charge in dust. In those cases where it is required to hasten the drying of a charge to an extent that, by the above-described arrangement, would cause the dust to rise, it is better to reverse the direction of the current, and by exhausting the air from the annular pipe, M, to create a current of

air over the surface of the charge, by means of a fanner or other suitable apparatus in connexion with the pipes, P, P; but the dust, then raised, is for the most part carried towards the openings, *m*, *m*, *m*, which should be covered with a thin woollen cloth, to prevent the ingress of the powder.

In constructing a mill in which this reversed current alone is to be used, the annular pipe, M, is made of greater size, and the apertures, *m* *m*, more numerous, and in such case no woollen cloth is placed over them, but the powder-dust is allowed to enter freely and pass along the pipe P^1, which is then made to terminate in a water-chamber, constructed on the plan of a Turkish water-pipe, so that the whole of the dust carried with the current along the pipe, P^1, is retained by the water. This ventilating pipe, M, might be arranged on the outer, instead of the inner, margin of the mill-bed, or the current of air (forward or reversed, as before described,) might be applied by an apparatus similar to that used for the application of the jets of steam; and the steam might be applied by this apparatus for the application of the current of air; but the arrangements above described are preferable, because it is desirable in all cases that the steam issuing from the steam-jets should impinge directly, and more or less forcibly, upon the charge; and, on the other hand, the air-current should not impinge upon it, but only pass gently over its surface.

Condensation of the Powder.

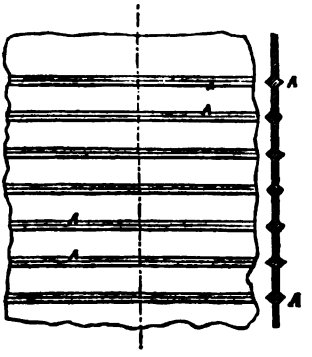
The mass removed from the mills after incorporation, is possessed of all the chemical properties of powder. It soon hardens, forming cakes of about three-fourths of an inch thick, which should have a dark greyish-black appearance and be perfectly homogeneous, exhibiting no specks whatever. In this state it is called *mill-cake*.

These cakes, before they are thoroughly dry, are reduced to coarse powder in the *breaking-down mill*, consisting of two sets of toothed metal rollers, between which the powder passes. It is then placed in layers of a certain thickness between copper plates, and packed in very stout boxes, in which it is submitted to a pressure of 122 tons on the square foot, by means of a powerful hydraulic press. When the powder is removed from between the plates, it presents very much the appearance of slate, being in very dense blackish cakes about $\frac{1}{2}$ inch thick: this is called *press-cake*. By subjecting the powder to this powerful pressure, its

density is greatly increased, and, consequently, a given bulk of the pressed powder will yield, on combustion, a much greater volume of gas than an equal bulk of that which has only been subjected to the pressure of the incorporating mill. Moreover, the hardness of the powder is increased in a similar proportion, so that it is better enabled to withstand the action of the atmosphere, and is less liable to loss, from dusting, in transport.

The copper plates used to separate the meal into layers, in the press-box, as above described, generally have smooth and even surfaces, and the press-cake has, therefore, a corresponding even surface. Mr. Willett, on the other hand, constructs these plates* with small ridges, A (Fig. 189), projecting from their surfaces, these ridges producing in the press-cake small corresponding indentations, as shown in the figure. The press-cake thus made, breaks very readily at these indentations, and is, consequently, more easy to granulate.

FIG. 189.



Another form of condensing machine, or *laminator*, consists of three rollers, through which the mass is passed in endless cloths. One of these surrounds the two upper rollers, the other the lower one only. A funnel conveys the paste between the cloths, with which it passes through the rollers, and appears at the other side in the form of a cake, which breaks off by its own weight and falls down. The cakes are at first 8 lines thick, and are reduced to one-fourth of their original thickness.

Granulation, or Corning.

All the processes above described, produce a cake which varies both as regards thickness and hardness; and this has now to be converted into grains, as that is the only form in which powder can be used. The reasons for this are many, and are all of equal importance. Why lumps and larger pieces cannot be used, requires no further notice: but it may be as well to state what advantages the granulated powder,—first introduced by the French,—has over the dusty or flour-like powder which was the only form

* Patented December 8th, 1857, No. 3042.

in which it was known prior to the 14th century. In the first place, powder-dust is inconvenient to handle, and colours too much; it also affords no guarantee for the constant relation of the proportions in the mixture. Again, when exposed to long carriage, not only would a larger portion be dispersed as dust, but the saltpetre and sulphur, which are much heavier, would sink to the bottom of the boxes or sacks, whilst the lighter charcoal would be left at the top. Moreover, experience has shown that a mass in dense grains attracts much less moisture than when it is in the form of fine dust. And lastly, the lesser degree of inflammability of the fine dust is a material point, *i. e.* when two equal charges of dust and grain-powder are fired, the latter burns much more rapidly, and has a proportionally greater action. In a mass of powder, the combustion proceeds, although with extreme rapidity, from particle to particle. This takes place either by means of the red-hot matters themselves, in which case it is much slower, or by means of the flame, provided sufficient space is left for it to penetrate the mass. The former is the case with dust, the latter with corned powder; when, therefore, only a few grains of the latter are ignited, the same action will result, on account of the flame spreading through the charge, as if the remainder had been ignited at several places simultaneously. According to the experiments of Piobert, with powder of density equal to 1·5, layers of 5·2 to 8 lines in thickness can be inflamed in a second, whilst with dust or meal powder, these layers cannot exceed 3·6 lines. The same is proved by the experiments made with percussion-caps: for the same charge carries farther when fired by a cap, than when flint and steel are used. Percussion-caps, therefore, effect a saving of powder for the same range: for the flame, which, upon the old plan with flint and steel, chiefly acquires an outward direction, can only escape, when percussion-guns are used, from the cap to the interior, or in the direction of the charge; it therefore penetrates with great velocity the interstices between the grains, and ignites, in the same time, a much greater proportion than could possibly be ignited by the spark from flint and steel. The action is, therefore, increased in the same manner as would have occurred, if the charge had been fired on the old plan from several touch-holes at once. Connected lumps of powder offer the greatest obstacle to the penetration of the fire; this is the case to such an extent, that powder in that state burns with a great evolution of sparks, but without

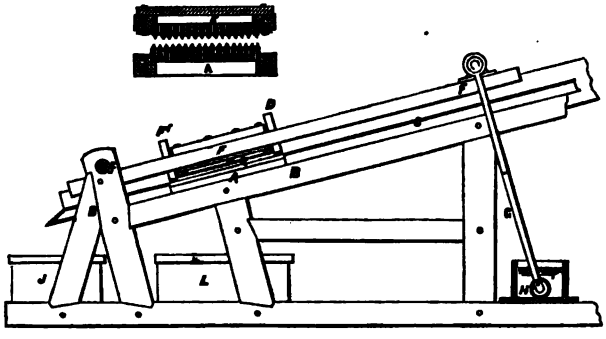
giving rise to a powerful explosion. With coarse-grained powder, the explosion is, therefore, weakened and less sudden. These facts are all known and are attended to in the adaptation of powder to fire-arms. For sporting purposes, where the barrels are most carefully made, of the purest and toughest iron, and consequently offer the greatest possible resistance, a more rapid explosion need not be feared. Sporting powder has consequently the finest grain. Cannon, on the contrary, are made of a more brittle material, which would more readily burst from any sudden explosion. Cannon-powder is generally made very coarse in the grain, and rifle-powder is intermediate between the two.*

Ordinary Process of Granulation.—The granulation consists in crushing the cake of powder into grains of about the size of coarse sand. Three kinds are always obtained, namely: grains of too large a size,—such as have the right dimensions (in several gradations),—and dust; these are separated from each other by sieves. It depends upon the use to which they are destined, whether these three kinds must be separated or left mixed, as they are in blasting powder.

Previously, however, to the actual granulation, the cake has to be broken up into coarse lumps, either with hammers, or by pressing it between metal ridges. A machine for this latter purpose has been patented by Mr. Willett.†

A A (Fig. 190), are the metal ridges forming the table which im-

FIG. 190. FIG. 191.



* Diminished quantity may replace coarseness of granulation, as will be seen below in a note relative to Captain Mordecai's experiments.—AM. ED.

† Date of Patent December 8th, 1857, No. 3042.

mediately supports the press-cake. These metal ridges are firmly fixed upon a strong and suitable wooden framing, B, on which they are placed at an inclination sufficient to cause the press-cake to slide freely upon their surfaces; C is a table covered with copper, and placed at the same inclination as the metal ridges A. The press-cake may be supplied to this table, C, from a hopper and endless band. The stop-board, D, is for the purpose of correcting any irregularity in the position of the press-cake as it passes on to the ridges, A, and also for stopping the passage of a fresh supply of press-cake while that which has been broken, is being discharged. E, E, are the pressing ridges, which are so adjusted that each lies evenly between each pair of supporting ridges. F^1 is a second stop-board to prevent the press-cake from sliding off the supporting ridges before it has been broken by the downward-pressing ridges, E, which are secured to the frame, F, moving upon the joint, *f*; the downward motion of this frame is caused by the connecting rod, G, which communicates with a crank, H, working in the box, I, which is filled with oil above the level of the crank. The ridges, A and E, are best made of copper, and of the form shown in Fig. 190, and for half-inch press-cake, it is advisable to make the distance between the parallel ridges of both A and E about three-quarters of an inch, and the distance of the surface of the supporting ridges from that of the downward-pressing ridges, about three-eighths of an inch. The action of this machine is very simple. The press-cake being supplied, as before stated, to the table C, passes by its own gravity to the supporting ridges A, upon which it is retained by the second stop-board, F^1; the other stop-board, D, is then closed, to check any further supply, and by means of the crank H, the upper ridges, E, are brought gradually down upon the charge, which is thus broken with a clean and even fracture, and yet but very little crushed; and as the ridges E rise from the charge, the greater portion of it will slide from the ridges A into the bin, J, as soon as the stop-board F^1 has been removed, and a small portion will also pass between the ridges A into the second bin, L. The press-cake, having been thus broken, is ready to be granulated by the processes now to be described.

At the Waltham Abbey works, a very ingenious piece of machinery is used for granulating the powder and separating it into the different kinds known as *large grain* (or L. G.), *fine grain* (or F. G.), and *meal-powder*, or dust, the last being always

worked up again under the mills, a proportion being added to fresh ingredients in the incorporating mill.

A continuous supply of the coarsely-crushed press-cake is allowed to fall upon a pair of revolving metal rollers, provided with large teeth, which reduce it to grains of different sizes; the powder, as it passes between these rollers, is received by a set of three long sloping screens or sieves of different fineness, fitted one upon the other, and working continually backwards and forwards, with a trough running their whole length at the bottom. The powder is thus subjected to a sifting motion; those portions which are retained by the first sieve, as they work their way down to its surface, are made to fall between a second pair of rollers with finer teeth; the powder granulated by these, again falls upon the upper screen, where it is once more sifted, and any portions that may still be too coarse to pass through, are reduced by a third and still lower set of rollers with finer teeth.

The powder, on passing through the first screen, falls upon the second, where the large-grain powder is retained, being separated from the fine grains and dust by the sifting motion to which it is subjected; the third sieve retains the fine-grain powder, while the dust or meal-powder falls into the trough beneath. Each kind of powder, as it travels down to the bottom of the screens, is collected at the opening in boxes running on wheels and rails. Various additional contrivances are applied to this machine, to obviate the necessity of the presence of the workmen during the granulation, in case of an accidental explosion.

After granulation, the powder is freed from dust, by allowing it to run gradually through sloping reels, enclosed in boxes and covered with canvas, or with silk of about 56 meshes to the inch, according to the size of the grains introduced.

The method of granulation adopted on the Continent is altogether different from the English method above described. The cake is first coarsely broken up with hammers, and then thrown into drum-sieves (Fig. 192) made of parchment or leather, in which round holes of uniform size are accurately pierced. A lenticular disc of hard wood, *t*, sometimes weighted with lead, is placed upon the sieve, together with the pounded cake. A rotatory movement is given to this by the workmen, and the lumps of cake are crushed with a slight pressure, until the grains are small enough to pass through the holes of the sieve. Sieves of

FIG. 192.

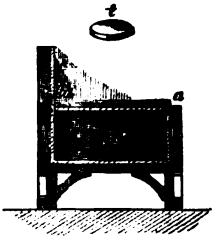


FIG. 193.

brass wire, and others of hair, serve to separate the coarser grains and the dust from the grains of proper size.

In the French works, the granulation and sifting of war-powder, prepared by the stamping process, is effected by means of three sieves, made as above described, but with holes of different diameter. The first, called the *guillaume*, has holes of 5 to 10 millimetres diameter; the second, or *artillery-powder granulator* (*grenoir de la poudre-à-canon*) has holes of 4 millimetres diameter; and the third, or *musket-powder granulator* (*grenoir de la poudre-à-musquet*) has holes of only 2 millimetres diameter.

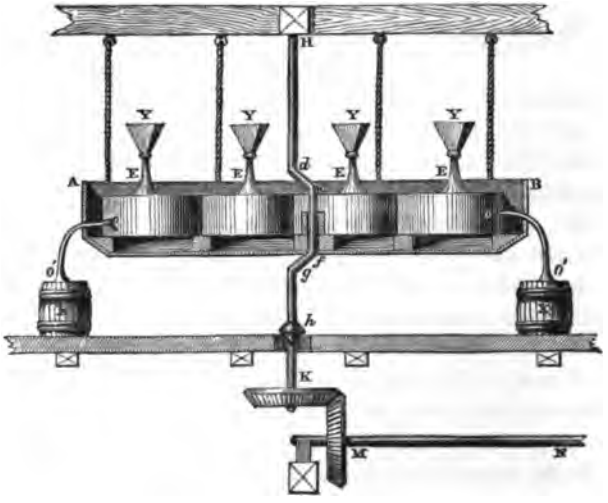
The sieves are worked over a number of wooden boxes, called *maies* (Fig. 193), placed round the interior of the granulating house, and having wooden bars, *a b*, placed across them for supporting the sieves. The workman having introduced the cake of gunpowder into the first sieve (the *guillaume*), together with the lenticular disc of wood above described, places the sieve diametrically on the bar, *a b*, and moves it backwards and forwards along the bar, always keeping it horizontal. This movement causes the wooden disc to travel constantly round the circumference of the sieve; and as, in consequence of its lenticular shape, there is always a portion of substance interposed between its surface and the bottom of the sieve, it presses the powder somewhat heavily and forces it through the holes of the sieve.

The powder which has passed through the *guillaume* is then placed in the artillery or musket-powder granulator, according to the kind of powder to be prepared. These sieves are worked in the manner just described with the assistance of the wooden disc. The powder which passes through the sieve is a mixture of grains of the required magnitude, of smaller grains, and of meal-powder. To separate the artillery-powder, the mixture is sifted through the musket-powder granulator, without the aid of the wooden disc. The finer grains pass through, and the artillery-powder remains on the sieve. The powder which has passed through, consists of musket-powder and meal. The former is separated by working the mixture on a sieve with smaller holes, the meal then passing through;

and by passing this through a sieve with still smaller holes, a certain quantity of fine grains may be separated, which may be sold as sporting-powder. The fine meal, which passes through all the sieves, is returned to the mill or mixed with a small quantity of water, and again worked upon the sieves.

Sporting-powder, which realizes a higher price, and admits of more costly apparatus being used in its manufacture, is granulated in France by a separate machine, consisting of eight sieves set in motion at the same time, but each granulating independently of the others. This apparatus consists of an octagonal wooden frame, A B (Fig. 194), 2·5 metres in diameter and suspended

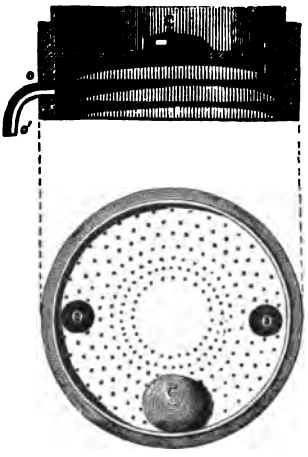
FIG. 194.



horizontally by eight cords. In the centre of this frame is a collar lined with copper, through which there passes a curved iron rod, *d e f g h*, called the *signole*; this rod forms part of a vertical shaft, K H, the upper extremity, H, of which turns in a socket fixed in a beam. The lower extremity, K, of the same shaft carries a horizontal toothed-wheel, fitting into a vertical wheel mounted on the horizontal shaft, M, by which motion is given to the entire machine.

On the frame, A B (Fig. 194), are fixed eight granulators (Fig. 195), each divided into three compartments by false bottoms. The first bottom, A B, is a plate of walnut-wood 2 centimetres

FIG. 195.



thick, and pierced all over its surface with small holes widened at the bottom. On this plate rests a lenticular wooden disc, C, weighing 2 kilogrammes; and at opposite points of the plate are two holes O, one decimeter in width, to which are adapted two inclined copper spouts, reaching to the second bottom, F G. This second bottom, fixed 3 centimetres below the first, is a metal plate pierced with holes of the size adapted to the grains of sporting-powder. Lastly, at the distance of 3 centimetres below F G, is a third bottom H I, formed of a hair-sieve which gives passage only to the fine meal. The lower surface of the granulator rests on the wooden frame, A B (Fig. 194), which is lined with leather; the upper surface is covered with cloth, to which is attached a leather sleeve, E, by which the powder is introduced. At the side of the granulator are two apertures, O O, to which are also fitted leather tubes for conveying the grain powder and the meal into small closed boxes, X X'.

The granulators having been arranged in the suspended frame (Fig. 194), the material is poured in through the funnels, Y Y, and the frame is set in motion. The wooden disc, C (Fig. 195), then travels round the wooden sieve, A B, and reduces the lumps to grains, which pass through the holes in AB, and fall on to the metal sieve, F G, the finer portion likewise passing through this and falling on the hair-sieve, HI, while the coarse grains remain on the metal sieve, and being thrown by the circular movement against the inclined spouts, pass up them, and are returned to the surface of the plate, AB, where they are again subjected to the crushing action of the wooden disc. At the same time, the mixture of fine grains and meal-powder which has passed through the metal plate, F G, to the hair-sieve, there undergoes a further separation, the fine meal passing through to the leather bottom, whence it is conveyed through a leather pipe to a small closed box, while the grain-powder which remains on the sieve escapes by an opposite opening into a small barrel With this machine, the workman has nothing to do but to pour a

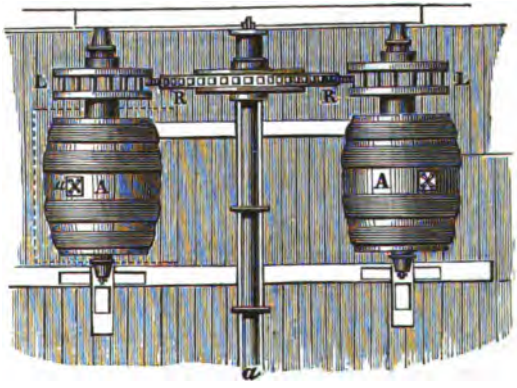
fresh supply of cake-powder into the funnels as soon as the noise of the wooden disc indicates that the sieves are getting empty. The meal-powder is returned to the mills, where it is moistened and submitted to fresh trituration, the cake thus produced being granulated as above.

Glazing.

All the processes hitherto described for the granulation of powder, afford only irregular and angular grains. They may, however, be rounded by a process called *glazing* or *polishing*, which at the same time renders the grains firm and shining, and prevents the powder from imparting colour to the touch. Sporting-powder is always glazed, but war-powder is mostly left unglazed, as its inflammability, already less than that of sporting-powder, on account of its larger grain, would be still further diminished by glazing.

A successful glazing operation requires that the powder should be moistened to a certain extent, which may be attained by previously drying it partially in the sun, or with greater certainty, by mixing a portion of dried powder with a sufficient quantity of the same kind undried. In this state, it is admitted through the flaps, *u u*, into the revolving barrels, A A (Fig. 196), which are

FIG. 196.



turned by a toothed wheel, R R, fixed to the long axis, *a*, of a water-wheel, and the shafts with drum-wheels, L L. Too much velocity would destroy the grains instead of polishing them: the barrels must therefore only rotate sufficiently to cause the grains to roll over each other, and become polished by attrition. The

barrels should only be one-third or one-fourth full, so that a barrel 64 inches long and 48 inches in diameter may contain 2 cwts. of powder; four rods are also fixed in each cask from end to end, to increase the friction.

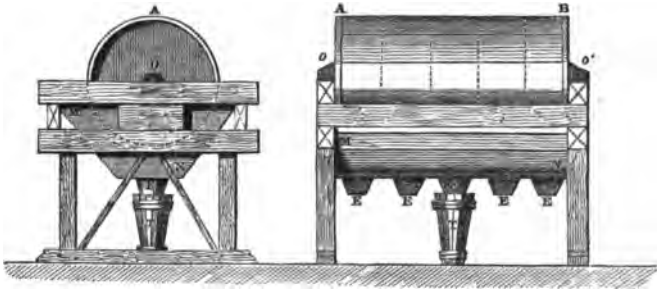
At first, the barrels are caused to revolve slowly, and the velocity is gradually increased. In France, for instance, where the glazing process lasts 36 hours, the barrels revolve, in the first 12 hours, from 9 to 10 times; in the second 12 hours, 30 times per minute; and in the last 12 hours, the velocity again diminishes. In England, the rotation is also slow at first, then for 5 hours, 38 revolutions are made per minute; in the next 3 hours, 20 revolutions; and at last, during 2 hours, the rotation is very slow. The diminution of velocity towards the end of the operation, is necessary to cool the powder, which becomes warmed up to 50° or 60° C. (122° or 140° F.), and in this state would lose much of its polish when exposed to the air. Glazed powder absorbs less moisture from the air, and can be better preserved, but with the firmness of its surface, the inflammability is diminished. For this reason, in Austria, the powder is removed from the barrels in about 8 or 10 hours, when it has acquired a dull lustre. It is remarkable, that the lower degree of inflammability noticed above, is compensated by greater density, and this increases with the humidity of the grain employed. Experiments made at Le Bouchet have very clearly proved this fact; it was found, that when compared with the weight of an equal bulk of water, the weight of a certain bulk of powder was:

Before glazing	0·810
After 4 hours' exposure in the barrels . .	0·833
„ 8 „ „ „ . .	0·846
„ 20 „ „ „ . .	0·869
„ 25 „ „ „ . .	0·870
„ 30 „ „ „ . .	0·889
„ 42 „ „ „ . .	0·893

The glazing apparatus used in France is represented in Figure 197. It consists of a wooden barrel 2·7 metres long and 1·20 metres in diameter, divided internally into five compartments, each having a separate door. The barrel turns upon a horizontal wooden axis driven by a cog-wheel connected with the prime mover of the machinery. The inner surface of the barrel, like that of the pulverizing drums, is fitted with twelve wooden ridges.

Above the barrel is a large hopper divided into five compart-

FIG. 197.



ments, corresponding with those of the barrel, and each terminating in a leathern pipe, which conveys the powder into the compartment of the barrel below it. Each compartment of the barrel is charged with 100 kilogrammes of granulated powder.

Blasting powder and very large-grained powder for rifled and heavy guns, are sometimes glazed with graphite. For this purpose the very finely-divided graphite prepared by Sir B. Brodie's process, viz. by subjecting graphite (especially the lamellar variety obtained from Ceylon) to the oxidizing action of a mixture of sulphuric acid and chlorate of potash, and heating the product to redness,—is far superior to the comparatively coarse powder obtained by mechanical grinding of the mineral. In the first place, it spreads over the grains of gunpowder in a much thinner film, so that a considerably smaller quantity of it is required, an important consideration when so costly an article is concerned. The saving thus effected was found to be no less than 50 per cent. in the experiments made on this subject at the Waltham Abbey works, under the direction of Mr. Abel, the chemist to the War Department, who anticipates a still greater economy in future trials with an improved apparatus. In the next place, it is found that the finer glazing opposes to the passage of the fire from grain to grain less impediment than the ordinary coarse glaze; so that, other things being equal, the finely-glazed powder is, for equal size of grains, more rapidly explosive. Thus, by the adoption of the improved glaze, a coarser granulation would probably be found to suffice for each of the varieties of powder to which the glazing is applied. The difference in the rapidity of explosion was ascertained by observing the propulsive effect of three portions of the same powder, one unglazed, one glazed with

Brodie's graphite, and one with ordinary graphite. The same proof-mortar and equal charges, were used in all the experiments; and the mean of six trials of each powder gave the following explosive rates, expressed in terms of the corresponding ranges :—

	Range.
Powder unglazed	353 feet.
„ glazed with Brodie's graphite . .	327 „
„ glazed with ordinary graphite .	295 „

Drying.

All freshly corned or polished powder is too moist for immediate use, and must consequently be dried. It is of importance that the firmness of the grain should not be destroyed by too rapid drying; and for the production of powder that does not easily absorb moisture from the atmosphere, gradual desiccation is also an important point.

The proper temperature for drying may sometimes be obtained in the open air, by exposure to the sun, or even in the shade, but this practice is inconvenient, on account of the changeableness of the weather and the hygrometric state of the atmosphere. Powder spread out upon drying cloths in layers of 1½ to 3 lines in thickness, and occasionally turned over, requires four hours to dry in the sun, at a temperature of 60° to 70° C. (140° to 158° F.), and nine hours in the shade where the temperature does not rise above 25° C. (77° F.). But a much safer plan is to dry the powder in a chamber heated by steam, in which the temperature is at first 19° C. (66° F.), and gradually rises to 50° to 57° C. (122° to 134° F.). An excellent method is adopted in France, where a current of air is driven by a ventilator through a box, in which it is warmed by steam-pipes traversing the box, and then permeates the woollen cloths containing the layers of powder 1½ inch thick, and forming, as it were, the lid of the box. In this manner, fresh dry air is continually passed between the grains.

Packing.—The finished powder is packed, either in sacks, which are placed in casks,—or in double casks, the inner one of which is pasted over with paper,—or, lastly, in tin canisters (sporting powder). For naval purposes, copper boxes covered with wood are employed. These packages hold quantities consisting of 1 cwt. or less.

Precautions against Explosion.—The greatest precautions are adopted to prevent accidents in the manufacture of gun-

powder, or, at all events, to prevent a fire in one part of the factory from extending to any other portion. Each process is conducted, if possible, in detached premises at some distance one from the other; and in some cases, these are flanked by high buttresses of brick or stone of considerable thickness. All kinds of grit are most carefully excluded from the various buildings, the floors of which are frequently covered with leather, and into which no person is permitted to enter in shoes that have been worn out of doors. Nevertheless, terrible accidents occur at times, the affinities between the constituents of powder being balanced with such nicety, that trifling causes, such as comparatively slight friction, are sometimes sufficient to impart to it the impulse necessary to its decomposition.

SPECIAL DESCRIPTIONS OF POWDER.

1. *Round-grained Powder, prepared by the Bernese or Champy Process.*

Blasting powder is prepared in France by a process originally employed at Berne, and introduced into France by M. Champy, director of powder-works, who greatly improved it. The same process is likewise used for the preparation of musket and ordnance powder.

As blasting powder ought not to possess a very high degree of inflammability, black charcoal is always used for its preparation. The sulphur and charcoal (30 kilogrammes of the former and 27 kilogrammes of the latter, which are the quantities required for 150 kilogrammes of powder,) are triturated together in an iron drawer with 120 kilogrammes of bronze balls (p. 398), half having a diameter of 4·5 millimetres, and the other half from 7 to 15 millimetres, the trituration being continued for four hours, at the rate of 25 to 28 turns per minute.

To every 14·25 kilogrammes of this mixture of sulphur and charcoal there is then added 23·25 kilogrammes of saltpetre, making in all 37·50 kilogrammes.

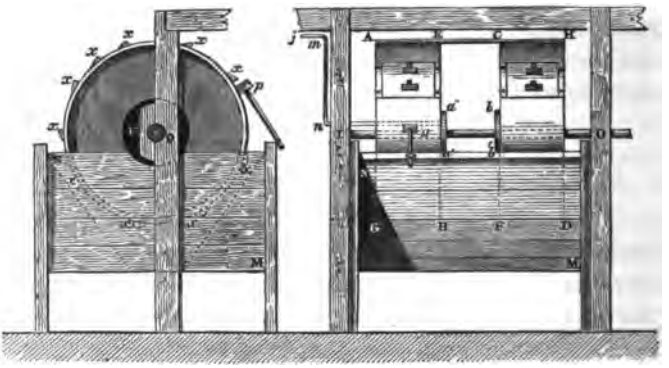
	Kilogrammes.	Percentage.
Nitre	23·25	62·0
Sulphur	7·50	20·0
Charcoal	6·75	18·0
	37·50	100·0

Each quantity of 37·50 kilogrammes is introduced into a pul-

verizing drum, together with 60 kilogrammes of copper balls 4·5 millimetres in diameter, and the drum is turned for four hours at the rate of 25 to 30 turns per minute. The mixture, which by this time has become very intimate, is then discharged into a trough, whence it is transferred in casks to the granulating house.

The machinery employed for the manufacture of round-grained powder consists of two large oak barrels, A E G B, C H F D (Fig. 198), 4·75 metres long, and 0·63 metres in diameter. One

FIG. 198.



end of each of these cylinders, E B, C F, is entire, the other ends, A G, H D, having circular holes, U, 0·60 metres in diameter at their centres.

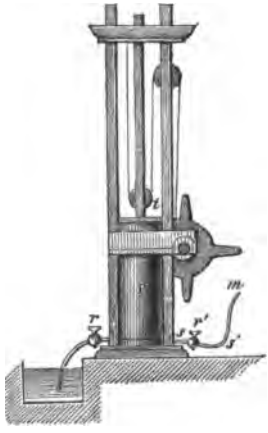
The two barrels are mounted on an iron axle, I O, supported on copper bearings between two stout beams, and fixed to the ends, E B, C F, of the barrels by the copper plates, *a a*, *b b*. Each of the barrels has a door, from 0·35 to 0·60 metre wide, secured by four copper bolts, and serving for the introduction and removal of the charges. The whole of the lower part of the apparatus is enclosed in a large trough, M N, furnished with inclined copper planes, which receives the charge when the doors are removed, and conducts it into casks placed below.

One of the cylinders, A E B G, serves for the granulation, the other, C H D F, for the glazing of the powder.

The outer surface of the granulator, A E B G, is provided with twelve small wedges, *x*, *x*, *x*, which, as the cylinder revolves, raise the hammer, P, and let it fall on the cylinder, thereby detaching any portions of the mixture that may adhere to the inner surface. A copper watering pipe, *m n*, 2 centimetres in diameter and 0·40

metres long, pierced with capillary holes along one of its edges, passes into the granulator, a little above the axis, and communicates by a curved copper pipe, *m s*, with a force-pump, P (Fig. 199), to the piston of which is fixed an iron rod, *t*, moving between two vertical beams of wood. The piston is raised by a handle and cord passing over a fixed pulley attached to the iron rod. On opening the cock, *r*, and raising the piston, the water rises into the lower part of the pump-barrel; and on subsequently shutting the cock *r*, and opening *r'*, the piston descends by its own weight and drives the water through the tube, *m n* (Fig. 198).

FIG. 199.



To commence the operation, the workman introduces into the granulator, by the door M, 100 kilogrammes of powder already granulated, this is called the *nucleus* (*noyau*): he then replaces the door and sets the granulator rotating at the rate of 10 turns per minute, moistening the charge at the same time, by the pump, with 5 per cent. of water. In this manner all the grains become uniformly moistened by the water falling upon them in the form of fine rain.

As soon as this sprinkling process is completed, 50 kilogrammes of the powder, as it comes from the mixing drums, is introduced through the door, U, by means of a wooden spatula, in quantities of 1 kilogramme at a time, care being taken to spread it uniformly on the bottom of the cylinder. The rotatory motion of the granulator causing the moist grains of the nucleus to roll continually in the midst of the dry meal-powder, the powder attaches itself to their surface, so that each grain increases in thickness by concentric layers.

The contents of the cylinder are then moistened a second time in the same way as before, after which, 50 kilogrammes of the meal-powder are again added by small portions, the granulator turned for about a quarter of an hour; and, the workman having ascertained that the whole of the fresh charge has been absorbed, the contents of the granulator are discharged into casks placed below. The entire operation occupies from 35 to 40 minutes.

The powder, as it leaves the granulator, is composed of grains of different sizes, and the next operation is the *equalization* (*égalisage*) of these grains. This is effected by sifting the grained powder through two leather sieves, the first called the *equalizer* (*égalisoir*) having holes 3·4 millimetres in diameter, and serving to separate the grains which are too large, while the second, called the *sub-equalizer* (*sous-égalisoir*), having holes 1·2 millimetres in diameter, serves for the removal of the smallest grains. After the powder has been successively agitated on these two sieves, the grains of intermediate diameter, which are adapted for blasting powder, remain on the sub-equalizer. The fine-grained powder which has passed through, serves for the *nucleus* of the next operation. At the commencement of a series of operations, when there is no round-grained powder to be had, angular powder, prepared by either of the preceding processes, is used as the nucleus.

The grains whose diameter is greater than 3·4 millimetres, which remain on the equalizer, together with the irregular lumps, are broken up by trituration with the lenticular disc of wood (p. 192), and serve also as nucleus in subsequent operations.

Blasting powder, prepared as above, is likewise glazed, by which its density is considerably increased. This operation is performed in the second cylinder C H D F (Fig. 198), 200 kilogrammes of the equalized grains being introduced into this vessel and turned for four hours. To ascertain when the powder has been brought by this treatment to the proper density, 60 grammes of it are taken out, exactly weighed, and then poured into a graduated measuring glass. The powder is known to be sufficiently glazed when the 60 grammes fill the measure up to a certain mark.

Lastly, the glazed grain is dried by the ordinary methods (p. 430).

Round-grained powder for military purposes is prepared in a similar manner, excepting that the proportions of the materials are different, viz.—75 saltpetre, 12·5 sulphur, and 12·5 charcoal as usual for French war-powder, and that two sizes of equalized grains are separated, viz.—of diameter between 1·2 and 2·1 millimetres for ordnance, and between 1·0 and 1·2 millimetres for small arms.

2. *Gunpowder prepared with Nitrate of Soda.*

It has already been stated that nitrate of soda is usually considered objectionable for the manufacture of gunpowder, on account of the facility with which it absorbs moisture from the air. According to some authorities, however, this hygroscopic tendency is altogether due to the impurities contained in ordinary Chili saltpetre, and when these are removed, the nitrate of soda is not more hygroscopic than nitrate of potash. Gentele, in fact, states that pure nitrate of soda may be kept in a damp cellar for months without absorbing moisture.

Mr. R. Oxland* refines nitrate of soda for the preparation of gunpowder by grinding the crude salt to powder, then placing it in a conical vessel, or in a vessel of the form of an inverted pyramid. The bottom of this vessel is pierced with holes, through which liquid flows into a receiver beneath. The ground nitrate is rammed down tightly into the vessel until full, and a quantity of water is then thrown or regularly distributed over the upper surface. The water, as it passes down, dissolves the chloride of sodium and other chlorides contained in the crude salt, and also some of the nitrate itself. A saturated solution of pure nitrate is then applied, and allowed to pass slowly through. The mass, when drained nearly dry, is taken out of the vessel and dissolved in water by the aid of steam, so as to form a saturated solution, to which carbonate of soda in solution, as pure as possible, is added as long as any precipitate is produced. The nitrate solution is then to be filtered, preferably through a set of filter-bags arranged in the same manner as in the refining of sugar. The purified solution of the nitrate may then be obtained in fine powder, by rapidly boiling it down in an iron pan, removing the precipitated salt as it settles to the bottom. The mass removed from the pan should be allowed to drain as dry as possible, and finally made quite dry by exposure to heat in a hot room, or on hot plates.

Pure nitrate of soda having been thus obtained, may be mixed with sulphur and charcoal by the ordinary methods. The following are good proportions for blasting powder :—

* Date of Patent, July 18th, 1860, No. 1740.

Nitrate of soda	85	parts by weight.
Sulphur	16	„ „
Charcoal (supposed pure) .	18	„ „
	119	

Coal-dust may be used as a substitute for charcoal, preference being given to that prepared from the most highly bituminous coal, and such as produces the smallest proportion of ash when burnt. The following are good proportions:—

Nitrate of soda	85	parts by weight.
Sulphur	16	„ „
Coal-dust	20	„ „
	121	

Messrs. Roberts and Dale, of Manchester, have patented* the addition of anhydrous sulphate of soda or magnesia (preferably the former) to gunpowder prepared with nitrate of soda, either alone or mixed with nitrate of potash, in order to correct the tendency of the nitrate of soda (unrefined) to become moist, the anhydrous salt taking up the water present, and incorporating it into its own substance as water of crystallization, so that it cannot show itself in the form of moisture. The proportion of anhydrous sulphate of soda added must not exceed 18 per cent. of the nitrate of soda present.

3. DAVEY'S *Blasting Powder*.†—In this powder, part of the charcoal is replaced by flour, bran, starch, or some other amylaceous or mucilaginous substance. This is said to prevent the explosion of the powder during granulation, for which operation the author proposes a new method. Chili saltpetre is dissolved in such a quantity of water, that the solution, when mixed with the sulphur, charcoal, and mucilaginous substance, may form a thick paste. This paste is kneaded to render it homogeneous, then passed between rollers, or through a wire sieve, the meshes of which are of the same size as the grains which it is desired to produce. The mass, thus divided into strips or long grains, is laid upon an endless cloth which carries it slowly through a drying chamber; it is then broken between wooden rollers, and thereby formed into grains.

* Dated January 18th, 1862, No. 139.

† Dingl. Pol. J., clvi, 78; Wagner's Jahresber., 1860, p. 208.

As nearly the whole of these operations are performed upon a wet mass, there is, according to the patentee, no fear of explosion. The powder thus prepared resembles the so-called *gunpowder tea*, but is without lustre. When used for blasting rocks, it is said to effect a saving of 37 per cent. in the weight of powder used, and moreover to be cheaper, weight for weight, because it requires less nitre, and the preparation is more expeditious. It is also said to produce less smoke, and to be altogether less dangerous than ordinary powder.

4. LANNOY'S *White Blasting Powder* or *Lithofracteur.*—This powder possesses the property of dislodging a rock without much shattering and without hurling the fragments to a great distance. It is a mixture of sulphur and saltpetre with a substance which performs the same function as the charcoal of ordinary powder, and appears to consist essentially of sawdust or bran. The preparation of this substance is a secret of the manufacturers (E. Lannoy and Co., of Brussels), but it is supposed to consist in treating the bran or sawdust with nitric acid, which, as is well known, converts all varieties of woody fibre into explosive compounds similar to gun-cotton, or pyroxylin. Lannoy's powder is moderately inflammable; a train laid with it and set on fire at one end burns very slowly, and goes out of itself, before the combustion reaches the other end. Hence the ordinary fuzes are not sufficient for igniting it, and it is necessary to employ a fuze which is split to the length of 4 inches at the end inserted into the charge, and tied in a knot.

5. A. de Trets* has taken out a patent for the preparation of blasting powder, composed of—

Nitrate of soda	52·5 parts.
Sulphur.	20·0 „
Washed tan	27·5 „

The nitre is dissolved by boiling in water, the tan is added to the solution, so as to be thoroughly impregnated; then the sulphur is added, after which the mixture is removed from the fire, well dried, and packed in bags or casks.

6. AUGENDRE'S *White Gunpowder.*—This powder is composed of—

* Repertory of Patent Inventions, February 1860, p. 142.

Crystallized ferrocyanide of potassium .	1 part.
White sugar	1 „
Chlorate of potash	2 „

The constituents are separately pulverized, and then mixed with the hand. In experiments with small quantities, as with a few grammes, the substances may be triturated together in the dry state in an agate mortar. In working with larger quantities, the mixture is moistened with 2 or 3 per cent. of water, and stamped in a bronze mortar with a wooden pestle. The inventor has for a long time used only bronze vessels. The mixture need not be made so intimate as with ordinary gunpowder, a quarter of an hour's trituration being sufficient on the small scale. It is granulated in the ordinary way and dried in the air.

This powder is white, and takes fire by contact with red-hot bodies or with flame, whether in the state of fine dust or granulated. It burns with a flame larger than that of common gunpowder, and leaves a smaller residue. It is perfectly inflammable as it comes out of the mortar, and there is no fear of the explosion failing under any circumstances. Unless very dry, it will not explode by the blow of iron upon iron. Neither is it inflamed by trituration between polished bodies, by the stroke of wood upon wood, or of wood upon metal. It is said to be superior to ordinary gunpowder in the following respects. It is composed of unalterable substances, and may, therefore, always be made of constant composition by weighing out the ingredients. Its constituents are not altered by atmospheric influences, so that it cannot deteriorate by keeping. The preparation takes but little time, and may be performed on the very theatre of war, the ingredients being separately pulverized, and mixed only when wanted, the danger of stirring up large quantities of material being thus greatly diminished. Its explosive power is much greater than that of common gunpowder, so that a greater number of cartridges made with it may be packed in a given space. Lastly, the dust acts just as well as the granulated powder; so that each constituent may be reduced by winnowing to a very fine powder, and the mixing performed in a rotating leather drum.

This powder has, however, the following defects: It oxidizes iron gun-barrels strongly, so that its use must be restricted to firing with bronze guns, and to the filling of hollow projectiles. It is much more easily inflammable than ordinary gunpowder, though less easily than other mixtures made with chlorate of

potash. Lastly, its high price must be a great obstacle to its general use.

7. *Davies' and Paine's White Gunpowder.*—A white gunpowder of similar composition has been patented in this country by John Davies and George Paine, of Truro;* it is prepared by mixing together

Ferrocyanide of potassium	¼ lb.
Chloride [? chlorate] of potassium	½ „
Crystallized sugar	2 oz.
Sulphur	1 „

Bucher's Fire-annihilator.—This is a composition containing the materials of gunpowder, but in different proportions, viz.:—

Nitre	63·73
Sulphur	28·93
Charcoal	3·80
Sesquioxide of iron	3·54
	100·00

The oxide of iron has but little to do with the combustion of the mass—and appears to be added merely to give it a red colour and the appearance of a new composition: at all events, the mixture is found to burn just as well without it.

The composition is much richer in sulphur than gunpowder, and therefore produces in combustion a considerable quantity of sulphurous acid. Supposing the charcoal to contain 80 per cent. of carbon, the products of combustion are probably:—

(*a*). *Gaseous Products.*		
Sulphurous acid	36·48	
Carbonic acid	11·70	
Nitrogen	9·10	
Hydrogen	0·07	
Aqueous vapour	0·81	
		58·16
(*b*). *Residue.*		
Sulphate of potash	14·23	
Sulphide of potassium	27·61	
		41·84
		100·00

* Date of Patent, March 30th, 1860, No. 824.

Hence a pound of the mixture should yield the following quantities of gas, estimated by volume at ordinary temperatures:

Sulphurous acid	2·36	cubic feet.
Carbonic acid	1·10	„
Nitrogen	1·36	„
Total . . .	4·82	„

The inventor recommends the use of one pound of the mixture for every 240 cubic feet of space—so that the quantity of gas evolved would be, at ordinary temperatures, about $\frac{1}{50}$th of the space on which it is to act. It must be remembered, however, that the gases will be greatly expanded by the heat of the combustion, and that the air of the room in which the mixture burns will also be greatly expanded by the heat, so that in fact it escapes with great force, and a whistling noise, from all the apertures of the room; so great, indeed, is this expansion, that unless a door be partly opened to give egress to a portion of the air, the window-panes of the room will be blown out.

The fire-extinguishing power of the mixture depends, not on the consumption of the oxygen of the air—since the mixture contains within itself the oxygen necessary for its combustion, but upon the production of large quantities of gases, especially sulphurous acid, which exert a direct extinguishing power on the flame. In closed or nearly closed spaces, this extinguishing power is very great, every flame in the space being quickly put out; but, as in other cases, the incombustible gases have no power to extinguish glowing pieces of wood—so that, although the fire may be put out while the space remains closed, it is very apt to burst out again as soon as air is re-admitted and comes in contact with the glowing wood.

A Commission appointed by the Hanoverian Government to examine and report upon the action of this fire-extinguishing mixture, do not speak very favourably of its efficiency in cases likely to occur. It is, as already observed, undoubtedly very effective in extinguishing flame in a room closed so as to prevent the entrance of fresh air; but in throwing it into a burning room, it would always be necessary to hold a door partly open, in order to give exit to the expanded air, otherwise, as before mentioned, the windows would be burst open, and the fire would immediately break out again; but the opening of the door would also give egress to such a quantity of utterly irrespirable gas,—that any

persons in the upper rooms of the house would be in great danger of suffocation: in fact, the effect of these suffocating gases, especially the sulphurous acid, would probably be more certainly fatal than even the flame itself. In factories and warehouses, this objection might not apply to the same extent; but in such buildings the annihilator would be less efficacious, on account of the size of the rooms and the communications between the different parts of the building, which it would be difficult or impossible to close. The only cases in which the Commission are of opinion that the mixture would be really efficacious, is in extinguishing the fire in a chimney, as the suffocating gases would then make their escape at the top, without incommoding the inmates of the house.

Phillips's Fire-annihilator.—This is a nearly cylindrical vessel, charged with a mixture of 20 parts charcoal, 60 parts nitre, and 5 parts gypsum. The materials are boiled together in water, and afterwards dried in a stove at 100° C. The whole is moulded into the form of a brick, down the axis of which there is a hollow cavity for the reception of a bottle containing a mixture of chlorate of potash and sugar, surmounted by a globule of sulphuric acid. The charge so prepared, is placed in a cylindrical vessel perforated in many places, and itself enclosed within another cylindrical vessel, also perforated for the passage of the gases; both these are contained in a double cylindrical receiver, the lower part of which contains a quantity of water. The apparatus is closed by two covers, in the outer of which is an opening for the escape of the vapour. In the centre of the cover, a spike is placed for the purpose of breaking the glass bottle deposited in the cavity of the charge. The spike, being forced down, breaks the bottle, and the sulphuric acid causes the instantaneous combustion of the chlorate of potash and sugar, which fires the charge. The gases now escape through the perforations, and heating the air in the water-chamber, and causing it to expand, force the water up a tubular passage into the space between and around the concentric cylindrical vessels. The water being thus converted into vapour, mixes with the gases and escapes by the discharge tube, forming a dense cloud which rapidly extinguishes flame.

When this apparatus was invented, about 20 years ago, great expectations were formed of its efficacy in extinguishing fires;

but they do not appear to have been fulfilled. In fact it is evident that the mixture is subject to the same objections as those previously noticed with respect to Bucher's fire-annihilator, excepting the production of sulphurous acid. The chief cause which renders all such mixtures comparatively useless, is doubtless the difficulty of permanently excluding the air from the glowing timbers, &c. after the flame has been extinguished.

PROPERTIES OF GUNPOWDER.

The outward appearance and character of powder afford a tolerably safe criterion by which to estimate its quality. It is generally slate-coloured, dark bluish-grey, or inclining to brown if the powder has been made with red charcoal (p. 391). A pure black colour indicates that the charcoal is either too hard or in too large proportion to the other ingredients. The colour should in every case be quite uniform; light spots, or glittering points, visible with the magnifier or the naked eye, prove a want of uniformity in the mass. This may have been caused by bad preparation from the beginning, or by the efflorescence of saltpetre on the surface when moist powder has been re-dried. Properly dried powder, when free from dust, ought not to colour the hand or paper; it should give a grating sound when squeezed together, and the grains should be difficult to crush. The powder, on being ignited in the open air, should leave as little residue as possible; and when it is burnt upon paper, the paper ought neither to be much blackened nor burnt.

Density.—The density of powder is one of its most important physical characters, on account of the great influence which it exerts on the inflammability and explosive force. It has to be considered from two different points of view; first, as regards the powder in mass; secondly, as regards the individual grains.

1. The weight of a given volume of powder (grains and interstitial spaces included), compared with that of an equal bulk of water, is called the *apparent* or *gravimetric density* of the powder. It is clearly upon this, that the volume of gas produced by the explosion of a given volume of the powder chiefly depends.

The gravimetric density is determined by weighing the powder in a measure of known capacity, filled exactly to the brim, by means of a tap-funnel fixed above it, and allowing the powder to fall slowly into it. The measure used in France is a litre; in

this country a foot-cube measure is used: whence the term "cubing" is applied to this particular mode of determining the density of powder. The difference between the weights of the measure full and empty, expressed in grammes, if the measure contains a litre, gives directly the apparent density of the powder, that of water being 1000. As a cubic foot of water contains very nearly 1000 ounces avoirdupois (accurately 997·1 ounces), the number of ounces of powder contained in the foot-cube measure, will give a near approximation to the apparent density of the powder; and the result may be rendered exact by multiplying it by the factor 1·003.

Determinations made on powders from all the powder-works in France, from 1819 to 1857, gave the following mean gravimetric densities:—

War Powder	for cannon	836
	for small arms	820
Sporting Powder	fine	923
	superfine	918
Blasting Powder		796

The operation of glazing greatly increases the apparent density of powder, by smoothing the asperities of the grains, and allowing them to approach one another more closely, the effect being greater as the grains are lighter and larger. For very light and large-grained powder, the increase of apparent density produced by glazing, varies from $\frac{1}{75}$th to $\frac{1}{15}$th; for ordinary powders it is, $\frac{1}{75}$th for blasting, $\frac{1}{90}$th for artillery, and $\frac{1}{150}$th for musket powder. The indications furnished by the preceding method depend indeed very considerably upon the form and regularity of grain of the particular powder examined. It need hardly be said, that powder of the same actual density may vary very considerably in apparent density, according as the grain is angular or round, large or small, or of mixed sizes.

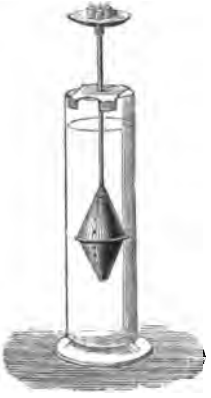
2. The *density of the grain* may be estimated with reference either to the apparent volume of the grain, or to its real volume, deducting the space occupied by the superficial cavities and pores. The former mode of estimation gives the *apparent density of the grain*, which greatly influences the bulk of the powder, its gravimetric density, and many of its properties; the latter gives the *real density of the grain*, which greatly affects the rapidity of combustion.

The apparent density of the grains may be determined by

direct measurement of their volume when they are spherical or of any other definite form; but in general, it is determined by immersing them in some pulverulent and incompressible substance, or in a liquid which does not easily penetrate the cavities: mercury, slightly warmed, is well adapted to the purpose.

The most convenient apparatus for this mode of determination is that invented by General Piobert, and represented in Fig. 200.

FIG. 200.



It consists of two hollow cones of sheet iron, joined base to base, the upper one being attached to the end of a thin steel rod, placed in the direction of their common axis, and surmounted by a small dish for holding weights. The apex of the lower cone is obliquely truncated and serves to introduce the powder; that of the upper cone is pierced with five or six small holes, which give egress to the air but prevent the passage of the powder. The instrument is placed in a glass jar containing mercury, and the steel rod is kept in the vertical position by passing it through a hole in the lid of the jar.

To make a determination, the instrument is first immersed empty in the mercury, previously warmed in a water-bath; the dish is loaded with a few grammes, sufficient to sink the instrument to within a few centimetres of the bottom of the jar; and its position is carefully marked. It is then withdrawn; a weighed quantity of the powder, well dried and free from dust, is introduced into it; the aperture is closed with the finger; the instrument inverted and again re-plunged into the mercury; the finger then withdrawn; and the instrument forced down to the bottom of the mercury. The greater part of the air contained in the powder then escapes through the holes in the upper cone; but a certain quantity always remains attached to the grains, and must be dislodged by forcibly agitating the instrument up and down, bringing it from time to time to the surface of the mercury. The lid of the jar is then put on, to keep the rod vertical, and the dish is screwed in its place and loaded with weights sufficient to sink the instrument to the same depth as before.

Let w be the weight required to sink the instrument to a certain depth before the introduction of the powder; w' that re-

quired to sink it to the same depth after the powder has been introduced, p that of the powder itself, and D the density of the mercury, then $w' - w + p$ is the weight of the volume of mercury displaced by the grains of powder. Consequently the apparent density of the grains is given by the equation

$$d = \frac{p\mathrm{D}}{w' - w + p}.$$

The mean apparent density of the grains of artillery powder thus determined, is 1·513; of musket-powder, 1·536; and of blasting powder, 1·425.

The *real density of the grains* of powder may also be determined by means of mercury; but it is necessary to subject the mercury to greater pressure, in order to force it into the cavities of the grains, or facilitate the escape of the air from these cavities by means of the air pump.

An apparatus in which this object is obtained by the simple pressure of a column of mercury, is that of M. Magnin, represented in Fig. 201. A vessel surmounted by two long glass tubes is weighed when full of mercury; it is then emptied; the powder is introduced; and the vessel is filled up with mercury till it stands at the same height in the tubes as before, and then weighed again. The difference of these two weighings, together with the weight of the powder itself, gives the weight of a volume of mercury equal to that of the powder, whence the specific gravity of the powder may be calculated as before. This instrument is, however, inconvenient, on account of the great weight of the vessel when filled with mercury, and the liability to fracture of the long tubes required to produce the pressure necessary for forcing the mercury into the cavities of the grains.

A more convenient apparatus, and that used by the English Government, is the *densimeter* of M. Mallet (Fig. 202), in which the air is partly expelled by exhaustion with the air-pump. It consists of an egg-shaped glass vessel with tubular extremities, each furnished with a cast-iron washer, on which is screwed an iron cap carrying a stopcock. Two diaphragms, one lined with chamois-leather for the bottom of the vessel, the other with very fine metallic gauze for the top, are placed at the junction of the washers and caps. To the lower cap is screwed a cast-iron jet with very fine aperture, by which the mercury is discharged from the egg-shaped vessel into a trough below. The

FIG. 201.

FIG. 202.

vessel communicates above with a barometer tube connected by a caoutchouc tube with an air-pump.

Three samples of 100 grammes each, of each of the powders whose density is to be determined, having been weighed out, the lower cock of the vessel is closed, the other two are opened, and the vessel and barometer-tube exhausted of air. The lower stopcock is then opened, and the mercury in the trough enters the vessel, fills it, and rises in the tube nearly to the barometric height. As soon as it has become stationary, the lower stopcock is closed and air is re-admitted into the top of the tube, till it exerts on the surface of the mercury a pressure of two atmospheres. All the cocks are then closed; the mercury trough is removed; the jet

unscrewed; the glass vessel with its caps also carefully unscrewed, taking care to hold it by the cocks or caps, and not by the glass; and the mercury which remains in the spaces beyond the cocks is allowed to run out. The glass vessel with its caps is then placed on an iron stand provided for the purpose; its outer surface is carefully cleansed; and it is then weighed: let its weight be w.

The glass vessel is now to be emptied of mercury by opening the cocks without removing the caps; the caps are then unscrewed, the diaphragms removed, and the vessel thoroughly cleansed inside and out; the barometer tube is likewise emptied of mercury.

The diaphragm lined with chamois-leather is now restored to its place, and the corresponding cap screwed on; one of the portions of 100 grammes of powder is introduced into the vessel by a funnel through the still open tubulure; the wire-gauze diaphragm and the corresponding cap are replaced, and the apparatus is mounted, connected with the air-pump, and filled with mercury under the same pressure as before, the mercury, as it rises, passing through the powder, filling its interstices and driving out the air. Lastly, the glass vessel with its caps is unscrewed and weighed as before; let its weight be w'.

From these two weights, together with the weight of the powder, the density is calculated in the same way as in the preceding cases.

The weight, w, of the vessel filled with mercury, is usually determined at the beginning, middle, and end of each series of experiments, the temperature of the mercury being noted at each weighing; and the mean of these three weighings is used as the value of w in the calculations relating to the whole series of experiments.

The weight w' is determined three times for each sample of powder, with the portions of 100 grammes weighed out at the commencement; and the mean of the three weighings is taken as the value of w' for each kind of powder.

These mean values of w and w', thus obtained, together with the weight of the powder used, and the density of the mercury determined at the mean temperature for each set of experiments, give the necessary data for calculating the real density of each sample of powder, viz.: by the formula—

$$d = \frac{p\mathrm{D}}{w - w' + p}.$$

where p denotes the weight of the powder used, and D the density of the mercury.

The *density of the mercury* used in each set of experiments, is determined in the usual way, by means of a specific gravity bottle, the bottle being weighed full of mercury and of distilled water at the same temperature. To calculate the density of the mercury at the temperature of the several samples of powder, it is convenient to reduce the density, experimentally determined, to that which the mercury would have at 0° C.

Let D_t be the density of the mercury determined at the temperature $t°$, D_o its density at 0°, D_{t_1} the required density at the temperature $t°$ of a sample of powder: then

$$D_o = D_t \left(1 + \frac{1}{5550}\right), \text{ whence } D_t = D_o \frac{5550}{5550 + t};$$

in like manner $D_{t_1} = D_o \frac{5550}{5550 + t_1}$.

The density of the mercury at $t_1°$ may also be calculated directly from its density at $t°$, by eliminating D_o between the last two formulæ, which gives

$$D_{t_1} = D_t \frac{5550 + t_1}{5650 + t};$$

but the use of the first formula, in which only the denominator changes with the temperature, renders the calculations easier when a number of determinations have to be made together.

An easier method of determining the real density of gunpowder, is, to weigh it in a saturated solution of saltpetre, the density of which has been previously determined. This method is not quite exact, because the solution, penetrating into the pores of the powder, partly destroys the grains; but it may be advantageously used when great accuracy is not required.

The following are the real densities of various kinds of powder:—*a*, as determined with mercury; *b*, as determined with a saturated solution of saltpetre.

	a	*b*
Artillery powder	1·535	1·615
Musket powder	1·540	1·654
Sporting powder, fine . . .	1·725	1·730
„ „ superfine .	1·790	1·795
„ „ extra fine .	1·875	1·823
Blasting powder	1·460	1·497

Inflammability of Gunpowder.

Although powder contains all the requisites for combustion (carbon as well as oxygen), yet it does not take fire at temperatures below a red heat. When the heat is cautiously and gradually raised, the sulphur first melts, and at last burns at a temperature of 150° C. (302° F.), as if it alone were present, and thus communicates the flame to the other constituents of the powder. If the air is withheld, and the heat is applied to the powder in a vessel void of air, the sulphur can not only be melted, but entirely distilled over. After the separation of the sulphur, the residue is affected as usual by the increase of temperature, the saltpetre melts, and is at last decomposed by the charcoal. Any sudden rise of temperature causes an explosion, just as if the experiment were made in the air. Powder is most rapidly and surely ignited by the contact of red-hot bodies, such as sparks of iron from a galvanic battery, glowing tinder, or when surrounded by a very hot flame (percussion caps). The phenomena observed by Hearder, not only with gunpowder, but with other similar mixtures, are exceedingly remarkable and difficult of explanation, should they be hereafter confirmed. He found, that powder exposed, in vacuo, to a platinum wire heated to redness by the passage of an electrical current, was not ignited. The sulphur melted and volatilized, just as if the powder had been slowly heated from below. A small quantity of air left in the vessel was sufficient to cause the explosion. The same occurred, and even more quickly, when nitrogen only was present, so that it would appear as if the ignition were dependent not merely upon the presence of oxygen but upon that of some gaseous body.

This subject has lately been more fully investigated by Abel,* whose experiments show, that when gunpowder is in contact with an incandescent wire in a highly rarefied atmosphere, the heat is, in the first instance, abstracted to so great an extent, by the volatilization of the sulphur, that the particles of powder cannot be raised to the temperature required for their ignition, until, at any rate, the greater part of the sulphur has been expelled from the mixture, in consequence of which, the portions first acted upon by the heat will have become less explosive in their character, and require therefore a higher temperature for their ignition, than

* Proceedings of the Royal Society, vol. xiii, p. 210.

in their original condition. The effect of the continued application of heat to the powder thus changed is to melt the saltpetre and establish chemical action between it and the charcoal, which, however, only gradually and occasionally becomes so energetic as to be accompanied by deflagration, because the gas disengaged by the oxidation of the charcoal, continues to convey away much of the heat applied, in escaping into the rarefied space. For the same reason, the grains of unaltered powder, which are in actual contact with the deflagrating particles, are not ignited by the heat resulting from the combustion, but are simply scattered by the rush of escaping gases. As the pressure of the air within the vessel is increased, this cooling effect diminishes, and the mode of combustion approaches more nearly to that which takes place under ordinary circumstances. When a few grains weight of gunpowder contained in a cup, were heaped over the voltaic wire bent down for the purpose, in an atmosphere reduced to 0·65 mercurial inch pressure, and the wire was heated to redness, three or four grains of the powder in immediate proximity to it fused in a short time, and appeared to boil, evolving yellowish vapours. After the heat had been continued for eight or ten seconds, those particular grains deflagrated, and the remainder of the powder was scattered by the explosion, without being ignited. Similar results were obtained under a pressure of one inch, but after the lapse of from ten to twenty seconds, three or four grains were deflagrated at once, the remainder being thereby projected from the cup. At a pressure of 1·5 inch, the same phenomena were observed, but the successive deflagrations of fused grains of powder followed more quickly on each other, and the final ignition of several together occurred in about ten seconds after the wire was first heated. At a pressure of two inches, only one or two of the fused grains were at first ignited singly; and several were deflagrated together after the lapse of five seconds. A larger quantity of the powder was burned, but a portion was projected from the cup, as in the preceding experiments. At a pressure of three inches, no grains were ignited singly; the combustion of the powder took place after an interval of about four seconds, and the greater portion was burned; but the combustion, though it had gradually become more similar to that of gunpowder in open air, was still very slow.

Experiments made with gunpowder in highly rarefied atmospheres of nitrogen, furnished similar results; neither was any important difference observed in the character of the phenomena

when oxygen was substituted for air, except that the scintillations and deflagrations of the powder-grains were, in some instances, somewhat more brilliant.

The preceding results of the retardation of the combustion of gunpowder in highly rarefied atmospheres, are quite in accordance with the retarding influence of diminished atmospheric pressure on the combustion of shell-fuses. It was observed by Quarter-Master Mitchell, an artillery officer stationed in India, that the fuses of shells burnt longer at elevated stations than when ignited near the sea-level; and subsequent experiments performed by Frankland* on the combustion of time-fuses in artificially rarefied air, and by Dufour,† on their rate of combustion in the open air at elevated stations on the Alps, have shown that *the increments of time of combustion are proportional to the decrements of pressure*, each diminution of one mercurial inch atmospheric pressure causing a retardation of one second in a 30-second fuse—that is to say, increasing the time of burning by one-thirtieth. This effect is easily explained when the mode of burning of the fuse is considered. The fuse burns only at a disc perpendicular to its axis, and the time occupied in its combustion depends on the rapidity with which each successive layer of the composition is raised to the temperature at which combustion takes place. Now this heat, necessary to deflagration, is derived from the products of the combustion of the layer immediately preceding; and the amount thus communicated to the still unburnt layer, depends, in a great measure, on the number of particles of these heated products which come into contact with that layer. Now, as a large portion of those products are gaseous, it follows —that, if the pressure of the surrounding medium is diminished, the number of ignited gaseous particles in contact at any one moment with the still unignited disc of composition, will also be diminished. Hence the slower rate of combustion in rarefied air.

The rapidity with which powder is ignited under ordinary circumstances, depends partly upon the relative proportion of its ingredients, partly on the mechanical nature of the mixture and partly on the character of the grain.

That kind of powder may be regarded as the best, which does not ignite too rapidly, and in which the ignition is, nevertheless,

* Phil. Trans., 1862, p. 629; Proceedings of the Royal Society, xi, 137—366.

† Compt. rend., lv, 796; Phil. Mag. [4], xxv, 156.

complete before the gases produced have had time to escape; that is to say, before the ball has left the barrel. Powder is often met with, which, from being badly prepared, burns too quickly, and is dangerous, from its tendency to burn the barrel of the gun. It is of the same character as the so-called detonating powder,—a mixture of 3 parts saltpetre (3 equivalents), 1 part carbonate of potash (2 equivalents), and 1 part sulphur (5 equivalents),—which explodes with a fearful report and blows the strongest vessel to pieces. The composition of this powder is such that sulphate of potash is formed, and carbonic acid and nitrogen are evolved in the proportions shown by the equation—

$$3(KO.NO^5) + 2(KO.CO^2) + 5S = N^3 + 2CO^2 + 5(KO.SO^3).$$

The quantity of gas thus produced is less than from an equal weight of ordinary gunpowder, but the danger lies in the extreme suddenness of its evolution.

The inflammability of dry gunpowder by a mere blow, without fire, is a well-known fact, and has more than once been the cause of accidents. That this property is not always due to an accidental admixture of other matters, as sand, &c., but is really a property of the powder itself, was proved by the experiments instituted at Freiburg with blasting powder made from chemically pure ingredients, namely 63·3 saltpetre, 20·0 sulphur, and 16·7 charcoal. Out of ten samples, which were wrapped in paper, and struck upon an anvil with a heavy hammer, seven of the corned powder exploded, and nine of the powder in the form of flour. Other kinds of powder behaved in the same manner. It is of importance, in the construction of powder mills, to know that the explosion occurs most easily by a blow from iron upon iron, iron upon brass, brass upon brass, even from lead upon lead, and lead upon wood, but not so easily from copper upon bronze or upon wood.

FIRING OF GUNPOWDER BY ELECTRICITY.*

1. *By the Voltaic Battery.*

The employment of electricity as an agent for effecting the ignition of gunpowder, suggested itself to Franklin in 1751, and to Priestley in 1767; but it was not till some years after the discovery of the electric pile by Volta, that earnest endeavours were

* Abel, "Quarterly Journal of the Chemical Society" (1861), vol. xiv, p. 165.

made to apply electricity to military and mining purposes. In 1832, the first experiments on the application of voltaic electricity in this direction, appear to have been made by French military engineers; about twelve years afterwards, that agent was first successfully employed in important blasting operations (such as, in England, the destruction of the Round Down Cliff, near Dover, and of the wreck of the Royal George, at Spithead), and from that period until very recently, the applications of electricity to mining purposes have been almost entirely confined to the employment of the voltaic current.

The original method of exploding gunpowder by the direct agency of the voltaic battery, and that still principally used in military operations, when the voltaic battery alone is employed, consists in causing the current (at the place where the powder is to be exploded), to traverse a short piece of fine wire, made of some metal of inferior conducting power, such as platinum or iron, which, in consequence of the resistance offered by it to the passage of the current, is raised to a red heat on completion of the metallic circuit of which it forms a portion. The thin wire is surrounded with fine-grain gunpowder, and is generally fitted into some simple arrangement, which may readily be connected with the circuit-wires, and brought into close contact with the charge to be exploded.

The other approved method of effecting the ignition of a charge of powder by a voltaic current, consists in the employment of an ingenious contrivance, first introduced by Messrs. Statham and Brunton, and founded upon an observation made in experiments with a submarine telegraph-wire which had been insulated with gutta-percha impregnated with sulphur. Some amount of chemical action is exerted between the sulphur and the copper, in covered wire of this description, in consequence of which, the surface of gutta-percha in contact with the wire, becomes coated with particles of subsulphide of copper, which remain attached to it on the removal of the wire. This coating of subsulphide is a sufficiently good conductor of electricity to assist the passage of a current of low tension across a small interruption in the metallic circuit; the heat resulting from the retardation of the current at such a point is, however, sufficiently intense to effect the ignition of some very combustible substance. It is obvious that this fact admits of ready application to the construction of an arrangement for the ignition of gunpowder, in which contrivance a hollow piece of gutta-percha, coated on the interior with the subsulphide of

copper, is made to replace the fine platinum or iron wire above referred to. The Statham fuze, constructed upon this principle, has been found, under favourable conditions, to present important advantages over the method of igniting gunpowder by means of fine wires.

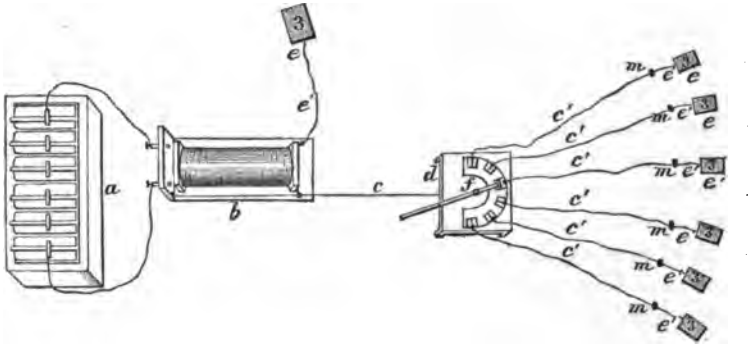
Although the employment of voltaic currents for the ignition of charges of gunpowder, obviously presents great advantages over the old system of firing mines or cannon, by means of slow and regular-burning matches or fuzes, its application, especially to military purposes, is attended with a considerable amount of uncertainty, due mainly to the great difficulty of ensuring a sufficient uniformity of action at different periods of time, even with the most efficient voltaic arrangements, and of securing the safe transport and proper preservation of any battery-arrangement, and of the agents necessary for its application;—also to the uncertainty of ensuring proper attention to the numerous little points, of vital importance to success, connected with such an application of electricity of low tension. Hence, almost ever since the first practical application of electricity to the ignition of charges of gunpowder, the possibility of rendering electricity of high tension available in this direction, and of applying to military operations the valuable discoveries of Faraday in electro-magnetism, has received, from time to time, serious attention on the part of military engineers and others specially interested in operations of this kind.

2. *With Electro-Magnetic Induction Apparatus.*

The first application, with practical success, of the form of electricity furnished by volta-induction apparatus to military purposes, was made in 1853 by a Spanish officer, Colonel Verdu, who succeeded, with the employment of only one element of Bunsen's battery, in exploding simultaneously six mines in one circuit, at a distance of 300 metres. This result was obtained by allowing the current to leap across small interruptions in the metallic circuits, which were surrounded with a readily inflammable substance, and imbedded in the charges of powder. The fuze employed was that of Statham, in which the terminals were surrounded by fulminate of mercury. Still greater results were obtained by arranging the mines in groups of five, so that each group formed a special circuit; by then bringing each circuit, in very quick succession, in connection with the instrument, the mines were all

discharged with a rapidity which had the practical effect of a simultaneous discharge. The reason for resorting to this method of operation is, that the discharge from an induction coil-machine, unlike that from a Leyden jar, which will pass through several hundred solutions of continuity, producing a spark at each interruption, becomes so enfeebled by successive interruptions in the metallic circuit, that it is impracticable to ignite, with certainty, a number of charges in one circuit, beyond certain limits, which, with the fuzes used by Colonel Verdu, were very narrow.

FIG. 203.



The arrangement of charges, &c., upon this system, is exhibited in Fig. 203, in which *a* and *b* represent the battery and coil-machine; *c*, the wire connecting one pole of the latter with an instrument, *d*, called a *rheotome*, provided with binding screws for receiving the separate wires *c'*, which lead to the mines *m*. These screws are fixed into small copper plates isolated from each other, being either let into the wood, or separated by strips of glass. The wire *c*, from the coil-machine, is in connection with a species of metal finger, *f*, which, by means of an insulating handle, may be made to describe a semicircle with optional rapidity; and, as one of its extremities presses firmly upon the instrument at a point near any one of the binding screws, it is brought alternately into contact with the several small metal plates with which they are connected, thus bringing them (and therefore the mines) into connection with the coil-machine. The wires *e'* and the plates of metal E, connect the charges and coil-machine with the earth.

A method of securing the practically simultaneous discharge of a number of mines, more effective than the so-called *rheotomic* arrangement of Colonel Verdu, was afterwards devised by

M. Savare, who appears to have first conceived the idea of dividing the circuit into branches, over the whole of which, a current, or rapid succession of currents, is distributed, on the completion of the circuit, with a uniformity regulated by the degree of resistance met with in each branch. Thus, on interposing one or more fuzes in each branch of the circuit, those which happen to offer greater facilities, in their construction, to the passage of the current, would explode first; and, the fuzes being so constructed that the terminals of the wires in them are forced apart by the explosion or fused by the heat generated, the further passage of the current in that direction is prevented, and the remaining fuzes are in their turn exploded. It is readily conceivable that, with the employment of currents of high tension, following each other with the enormous rapidity with which they pass off from the coil-machines, the discharge of a number of fuzes may be effected by the above arrangement with a rapidity which has practically the effect of a simultaneous discharge. Experiments with this mode of discharge were made at Grenelle in 1854. The arrangement of charges, discharging instrument, connections, &c., is the same as in Figure 203, excepting that the branch-wires are connected with the wire *c*, leading to the machine, instead of by the agency of a rheotome.

In 1856, an extensive series of experiments was undertaken by Professors Wheatstone and Abel, by desire of the Secretary of State for War, for the purpose of testing the relative advantages offered by electricity of high tension obtained from different sources, as applied to the explosion of gunpowder. Their first endeavours were directed to ascertain what description of priming materials are best adapted for employment in fuzes to be used with the volta-induction current, and the maximum number of charges which could be fired with certainty by means of a coil-machine and a battery of moderate power. A Ruhmkorff's coil of considerable size was employed, charged by a battery of cast-iron cells and zinc plates (the latter 5 inches by 3 inches); and in most of the experiments, the current was made to pass through one mile of copper wire (No. 16 gauge), insulated with gutta-percha, the metallic circuit being in many instances interrupted by an earth-connection about 200 yards in length.

The results of a large number of experiments were as follows:

Fine-grain or meal gunpowder was found to be ignited readily

by means of the induction-coil, with the employment of one cell of the battery. Numerous substances of a more highly explosive character were tried, alone, and in admixture with gunpowder. The best results were obtained with fulminate of mercury. The efficacy and delicacy of the fuze were also found to depend in very great measure upon a proper adjustment of the wire-terminals which it enclosed.

The number of charges placed in succession, in single circuit, which could be fired at one time by means of such coil-machines as those used, and with the employment of twelve cells of the battery specified above, did not exceed eight (and was generally below that number) even when priming compositions of a sensitive character, containing fulminate of mercury, gun-cotton, sulphide of antimony and chlorate of potash, &c., were employed. The discharge of this number could not, however, be relied upon with certainty; and the employment of twelve cells did not appear to offer any decided advantage over the use of only four. The ignition of two charges could be effected, almost with certainty, by the employment of only one cell, and the result appeared to be rendered certain by the use of four cells.

By employing a rheotomic arrangement for changing the direction of the current, so as to bring wires connected with one or more charges successively into the circuit (as previously described), a considerable number of charges could be fired in very rapid succession. This result was, however, perfectly certain, only when a single charge was brought into the circuit at one time.

Upon employing M. Savare's arrangement of branch-circuits (p. 456), five or six charges were exploded at one time, and a far more considerable number ignited, with a rapidity almost instantaneous. This method of exploding a number of charges at once, or in very rapid succession, is undoubtedly more efficient than the best rheotomic arrangement, and it renders the operator independent of the uncertainty of firing three or four charges simultaneously, when arranged in a simple circuit; for, in the latter case, if the ignition of the whole number is not perfectly instantaneous, the explosion of the first prevents the discharge of the remainder; while, in the arrangement just referred to, the connection of each fuze with the instrument is independent.

In the course of these experiments, considerable irregularity was observed in the power of the same machine at different periods, although the battery-power employed was, to all appear-

ances, the same on each occasion,—an irregularity which must be ascribed to defective insulation, arising from the deposition of moisture on some portion of the apparatus. It was found that the arrangement attached to the coil-machine, known as the condenser, and upon which the intensity of the current produced greatly depends, was very liable to be put out of order in the transport of the apparatus, and by other trifling causes; any derangement of this part of the apparatus was fatal to its efficiency. The perfect insulation of each coil of the secondary wire and other somewhat delicate portions of the apparatus, were also found liable to injury from a variety of sources, which it would be very difficult to guard against in the employment of coil-machines for field purposes, and by persons not thoroughly acquainted with their somewhat complicated construction and their action.

Although, therefore, the system of exploding charges by means of the induction coil machines, offers several very important advantages over the voltaic battery employed alone (one of the principal being the great reduction effected by its use in the power of battery required), its adoption as a general substitute for the old system of operation with the battery, cannot be recommended with confidence, principally because proper reliance cannot be placed upon the certainty and permanent uniformity of action of the apparatus.

Much more satisfactory results are, however, obtained by the use of more powerful induction-coils of recent construction, especially when combined with the phosphide of copper fuze to be hereafter described (p. 461).

3. *By Friction-Electricity.*

The very high tension of friction-electricity, and the consequent facility with which the discharge will pass through a considerable number of interruptions in the metallic circuit, render it well adapted to mining and engineering operations in which a number of charges have to be fired at once. Moreover, the simplicity and portability of the apparatus are greatly in its favour, as compared with the volta-induction apparatus, or indeed any other in which voltaic-batteries have to be used. An essential condition of success, however, difficult to fulfil in many cases, especially in field operations, is to keep all the insulating parts of the apparatus warm and dry.

In 1853, the Imperial Engineer Academy of Austria devised a

system of exploding charges by friction-electricity, which appears to have furnished very important results, and to have been frequently applied to industrial operations.

The electric machine employed is arranged in a very portable form, and consists of two discs of polished glass, 12 inches in diameter and four lines thick, fixed upon one axis, within 1½ inches of each other, and fitted with cushions to which springs are attached. The Leyden jar is cylindrical, 15 inches high and 6 in diameter (its area being 276 square inches). It is protected by flannel and fixed in a case of lacquered tin, being screwed on to an iron plate which is connected with the friction apparatus. The charging is effected by means of a steel point, which projects one inch into the space between the discs, and can be pushed into an arm of the conductor. The latter is inserted into a plate of hard caoutchouc which forms the cover of the Leyden jar, and is connected by chains with its inner surface. The machine is always covered, when in use, with a case, the sides of which are made of thick leather, and the top of tin. A small stove is also fixed beneath it, so as to dry the air inside when necessary. The wire employed as conductor is brass, which is raised on insulated posts or covered with gutta-percha. The priming material used in the fuzes was, first, fulminate of mercury; a mixture of chlorate of potash and sulphide of antimony was afterwards adopted. A large number of experiments were tried with this arrangement, under the various conditions in which it might receive application. The greatest distance at which an inflammation was attempted, was four German miles. On several occasions, fifty mines were simultaneously discharged in the same circuit; the fuzes were two klafters (toises) from each other, and the electric machine was 140 klafters from the nearest fuze. In like manner, thirty-six charges were simultaneously exploded in one of the branches of the Danube; these charges were placed six feet under water, and had remained submerged during twenty hours previous to their explosion. Other operations on a large scale, in marble quarries, in the beds of rivers, &c., in which considerable masses of matter were displaced, place the efficiency of the process beyond doubt. The objections to the system are, that some scientific skill is required in the manipulations; that great care is needed in the preservation of the apparatus;* and that the in-

* Since the account of the above experiments was published, very portable and perfect electrical machines (with accumulators attached) have been

ductive action is sometimes so energetic, that explosions are occasionally determined in other mines not intended to be included in the series, and not connected with the machine.

Messrs. Wheatstone and Abel have made a series of experiments for the purpose of ascertaining whether Armstrong's *hydro-electric machine* might not be advantageously substituted for the ordinary electrical machine, for charging a Leyden jar on the field. The results of these experiments show that, for general field-service, the hydro-electric machine cannot be safely relied on, chiefly on account of the difficulty of sheltering it from the wind, which interferes with the action of the steam-jet; but that in mining operations of an extensive character, such as the destruction of docks, bridges, &c., where it is desirable to ignite a large number of charges simultaneously, and where full appliances are at command for sheltering the apparatus, keeping the jars dry, &c., it is susceptible of very effective application.

4. *By Magneto-Electricity.*

The ignition of gunpowder by the direct application of a magneto-electric current has never yet been practically applied to military or industrial operations; but the experiments of Messrs. Wheatstone and Abel have shown that it is capable of fulfilling every condition required for such purposes. In the first experiments, a very large powerful magneto-electric machine was used, the armature of which was suddenly detached from the magnet by means of a lever. It was soon found, however, that even with this instrument, gunpowder itself could not be ignited with any degree of certainty. Results obtained with Statham's and other fuzes, though superior to those furnished by gunpowder alone, were still far from satisfactory. Experiments were therefore made, in the first instance, with the view of discovering a suitable priming material. The following were the principal compositions tried:—mixtures of meal powder with powdered coke, with sulphur, with sulphur and iron filings, with iron filings and carbon, with fulminate of mercury, and with the latter in addition to iron filings and to coke; fulminate of mer-

constructed in Austria of vulcanite. Abel has found that these machines are very effective, and that their efficiency is not interfered with, even by very damp or wet weather. He finds them much superior, for *extensive* mining or blasting operations, to any magneto-electric machine hitherto constructed.

cury (percussion-cap composition), alone, and with coke; detonating composition (sulphide of antimony and chlorate of potash); the same mixed with iron filings and with coke; gun-cotton alone, and mixed with some of the above; amorphous phosphorus in admixture with oxidizing agents.

Many of these compositions furnished results, to a certain extent favourable, a number of fuzes, primed with them, having been fired in succession with the magnet; and from two to four charges in one circuit having been ignited, in a very few instances. But no perfect certainty of discharge was attained with any one of the above materials, the attempt to fire a fuze being frequently unsuccessful, while no difference between it and a successful fuze containing the same composition, could be detected by careful examination. These preliminary trials, however, established the fact that the sensitiveness (ready explosiveness) of a priming material was not alone sufficient to determine its success, but that those which possessed a certain, though not too considerable, degree of conducting power, were more readily and certainly ignited than others of a far more sensitive character.

It was also found, that the impregnation of ordinary gunpowder with a small amount of moisture, rendered its ignition, by means of the magnet, a matter of certainty.

After a considerable number of experiments, Mr. Abel succeeded in preparing a priming material for the fuze, greatly exceeding in sensitiveness any of the other compositions hitherto tried. This priming composition consists of a very intimate mixture of subphosphide of copper, chlorate of potash, and levigated coke, the latter substance being employed to add to the conducting power of the mixture, which was found otherwise insufficient.

In the course of experiments subsequently carried on with fuzes containing this composition, it was found that a slight residue, consisting principally of the coke employed, occasionally remained on the surfaces of the terminals in the fuze, after its discharge, and, by forming a good conducting link between them, interfered with any future effects of the magnetic current in other directions, by the establishment of a complete circuit. This obstacle was entirely removed by substituting, for the coke, another material, more easily acted on by the chlorate of potash, and answering equally well as a conducting medium, namely, the subsulphide of copper. No instance has occurred, in the discharge of several thousand fuzes primed with the mixture of subphosphide and

subsulphide of copper with chlorate of potash, in which the terminals have not been found quite free from adherent residue, after the ignition.

The subphosphide of copper, which is produced at an elevated temperature, is a compound of very stable character; and the mixture of the three constituents is quite as unalterable as the explosivè mixtures which are in general use for the preparation of percussion caps, &c. Fuzes primed with it, have been found to retain all their delicacy and certainty when tried more than two years after preparation.

The efficiency of this priming material, as indeed of all others, depends, however, essentially on the due proportioning of the ingredients, so as to ensure the requisite degree of conducting power without too great diminution of sensitiveness. If the proportion of subsulphide of copper is too small, the mixture does not possess sufficient conducting power, so that, if the magneto-electric machine employed is not very powerful, or if the resistances are considerable, the current will not pass at all; and, on the other hand, if the proportion of subsulphide is excessive, the mixture conducts too easily, and the current passes through the fuze without igniting it.*

The fuzes contrived by Abel for use with magneto-electric apparatus are of two kinds, the one being adapted for mining purposes and the other for firing cannon. The fuze for mining purposes (Fig. 204) consists of,—

a. A head, for receiving the wires which connect the fuze with the magnet and the earth;

b. The insulated wires, with the terminals of which the priming material is in close contact;

c. A small cartridge or charge of powder, enclosing the terminals, upon which the sensitive composition rests.

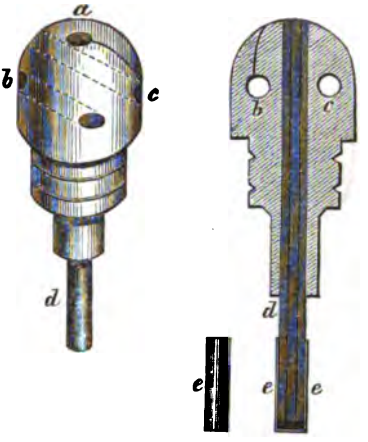
The wooden fuze-head contains three perforations (*a a*, *b b*, *c c*, Fig. 205); the one, passing downwards through the centre, receives about two inches of double insulated wire, *d*.† The other two

* Abel's fuzes, as now sold, are suited, by slight modifications in the conducting property of the priming composition, for employment with electricity both of high and low tension. The electrical time-guns which have been established in the North, and even in Australia, are fired with Abel's fuzes, some being ignited by magneto-electricity, and others by voltaic electricity.

† This double covered wire consists of two copper wires of 0·022 inch

FIG. 204.

FIG. 205.



perforations, which are parallel to each other on each side of the central one, and at right angles to it, serve for the reception of the circuit-wires. The arrangement for securing the connection of these with the insulated wires in the fuzes, is as follows:—

The piece of double covered wire above referred to, is originally of a sufficient length to allow of the gutta-percha being removed from about 1½ inch of the wires. These bare ends of the fine wires, which are made to protrude from the top of the fuze-head (*a*, Fig. 205), are then pressed into slight grooves in the wood provided for their protection, and the extremity of each is passed into one of the horizontal perforations in the head, in which position it is afterwards fixed by the introduction, into the hole, of a tightly-fitting piece of copper tube, so that the wire is firmly wedged between the wood and the exterior of this tube, and is

diameter, enclosed side by side, at a distance of $\frac{1}{16}$ inch apart, in a coating of gutta-percha of ¼ inch diameter. It has been prepared by the Gutta-Percha Company, for this particular purpose, in considerable lengths (300 yards), from which the pieces of requisite length are cut off as required. The insulation of the two wires has been found perfect throughout the whole length manufactured at one time.

thus at the same time brought into close contact with a comparatively large surface of metal. It will be seen that it is only necessary to fix one of the circuit-wires into each of these tubes in the opposite sides of the fuze-head, in order to ensure a sufficient and perfectly distinct connection of each one of them with one of the insulated wires in the fuze.

FIG. 206.

The phosphide of copper fuze for firing cannon (Fig. 206) differs somewhat in construction from the mining fuze. The head is somewhat longer, and of such a form that the double-covered wires are completely enclosed in it, the lower extremity of its central perforation still remaining free to receive the top of the quill or copper tube, which is charged with gunpowder in the same manner as the ordinary tube-arrangement for firing cannon.

Numerous experiments, made with the aid of the detonating mixture with which these fuzes were primed, established the fact, that the current obtained by means, even of a very powerful magneto-electric machine, when applied to the ignition of several charges arranged *in succession* in one circuit, is very limited in its powers. In illustration of this, it may be stated that, on trial being made of twenty-one consecutive sets of four charges, eighteen of the sets were perfectly discharged, but in the other three sets, only two or three of the charges were ignited. Out of five sets, of five charges each, only two sets were completely discharged; and in several attempts made to ignite six fuzes in one circuit, only four were fired in each case. In all these experiments, when charges had escaped ignition, the current had passed through the sensitive composition without firing it. When the discharged fuzes were removed, and the remaining ones properly connected, they were all fired. The result was not affected by modifying the proportions of ingredients in the priming composition, so as to diminish or increase its conducting power. Three charges might, therefore, be considered the largest number that could be ignited *with certainty* by means of a powerful electro-magnetic machine, when they were arranged in succession, in simple circuit.

The plan originally suggested by M. Savare (p. 456), of ar-

ranging the charges in divided circuits was next tried, and furnished far more successful results. The simultaneous ignition of twenty-five charges, thus arranged, was repeatedly effected; and forty charges were similarly exploded on several occasions. These results were all obtained with the large magnet above mentioned (p. 460), the current being established by rapidly separating the armature from the poles by means of a lever. By a simple arrangement for shifting the connection of the main wire with the exploded charges, from them to a second series similarly arranged, twenty-five were almost simultaneously ignited on allowing the armature to return to the poles of the magnet. It was found, moreover, that the same number could be fired by means of this magnet, even if two folds of thick brown paper were interposed between the poles and the armature, so that, on depressing the lever, the armature had no longer to be forcibly detached, but simply to be removed from the magnet. The success of these results led to trials of magneto-electric machines of comparatively small size, with revolving armatures. With a small horse-shoe magnet, 7 inches in length, 1 inch in breadth, and $1\frac{3}{4}$ inches in thickness, provided with a revolving armature and multiplying wheels, by which great rapidity of motion could be attained, twenty-five charges were fired; the effect of the discharge on the ear was, however, not like that of one single explosion, as was the case in the former experiments, but like that of an exceedingly rapid volley, in which the explosion of any single charge could not be distinguished. Still more favourable results were obtained with a very compact arrangement contrived by Professor Wheatstone, consisting of six small magnets, to the poles of which are fixed soft iron bars, surrounded by coils of insulated wire. The coils of all the magnets are united together, so as to form, with the external conducting wire and the earth, a single circuit. An axis carries six soft iron armatures in succession before each of the coils. By this arrangement, two advantages are gained; all the magnets simultaneously charge the wire and produce the effect of a single magnet of more than six times the dimensions, and, at the same time, six shocks or currents are generated during a single revolution of the axis, so that, when aided by a multiplying motion applied to the axis, a very rapid succession of powerful currents is produced. A single large magnet with a rotating armature could not be made to produce the same succession of currents, without the application of con-

siderable mechanical power. Another peculiarity of this apparatus is, that the coils are stationary, and the soft iron armatures alone are in motion: by this disposition, the circuit is never broken during the action of the machine. In the usual magneto-electric machines with rotating armatures, the circuit is necessarily broken twice during every revolution; and this frequently gives rise to irregularities in the production of the currents. By the construction just described, the currents can never fail to traverse the circuit.

By means of this apparatus, twenty-five charges were frequently fired in divided circuit, with such rapidity that the effect on the ear was as of one explosion, only of slightly longer duration than when the large magnet was employed. On some occasions, when a slight difference was made in the velocity with which the apparatus was worked, an interval could be distinctly noted between the first and last discharge, but even in those instances, the effect could not be considered as otherwise than a practically simultaneous discharge. Some sets of fifty charges in divided circuit were also ignited by means of this apparatus; but in those instances, the interval between the first and the last discharge was naturally longer, being about the same as that observed when twenty-five charges were fired by means of the small magnet above mentioned.

The connection of the magneto-electric apparatus and of the fuzes with the branch wires of the circuits, and with the earth, are easily effected by means of copper wires—the tension of the current being high enough to render unnecessary the tedious operation of brightening every metallic connection, so essential when the voltaic battery is used. For the details of the modes of making these connections, we must refer to the original memoir.

Force of Powder.

The knowledge of the force exerted by ignited gunpowder—a force capable of blasting the firmest rocks, and of propelling a four-and-twenty-pound ball with greater velocity than that of sound*—would, doubtless, be a very important addition to science, and to the practice of artillery and blasting; unfortunately, however, the only two methods of ascertaining this, viz., calculation and

* Sound travels at the rate of 1130 feet, the ball at the rate of 1404 feet in the first second.

direct observation, are both somewhat uncertain. By this force, we understand nothing more than the pressure exerted by the gases evolved on ignition, upon the bodies in their immediate vicinity (the sides of the barrel). To calculate this force, and compare it with the pressure of the atmosphere, it would be necessary to know:

1. The quantity of gas produced from a given amount of powder,

2. The temperature of combustion, and

3. Whether the gases, at that high temperature, expand in the same ratio as at lower temperatures.

Of the two latter points we know but little; it may, however, always be assumed that the temperature is at least between 1000° and 1200° C. (1800° and 2160° F.). The amount of gas produced is likewise not known with certainty, and doubtless varies with the circumstances of the combustion. Although it may be calculated what amount of space the nitrogen, carbonic oxide, or carbonic acid of a given charge of powder will occupy, yet it must be borne in mind, that the powder always contains moisture, and that the aqueous vapour,* and the products of decomposition to which it gives rise with carbon, will exert an influence, as well as the sulphide of potassium, and other solid products, which, doubtless, assume the form of vapour at that high temperature. To what extent the volume of gas is augmented by the aqueous vapour and these volatilized products, it is not possible to estimate. These irregularities explain why such different results have been obtained, on collecting and measuring the gas; thus, there have been obtained from 1 measure of powder:

Robin.	Saluces.	Hawksbee.	Gay-Lussac.	Brianchon.
244	264	232	450	400

measures of gas, which gas, being measured cold, does not include any aqueous vapour or sulphide of potassium, &c.

Besides, there are two other influential circumstances which cannot be included in the calculation. The first of these is the air, which is enclosed with the charge, and expands by the heat with the other gases evolved from the powder, and augments the

* Rumford took great pains in his time (1800), to prove the unfounded assertion, that the action of powder depended solely upon its moisture, *i. e.* upon the sudden formation of aqueous vapour; according to which, there would be none but steam guns and steam cannon.

action to such an extent, that when the pellet or the ball is not tightly rammed down, the barrel often bursts; in blasting, this circumstance has been made use of with a great saving of powder;* the second is, that all the powder is never consumed, but partly expelled with the ball. Rumford has shown, that a ball of powder (instead of a leaden ball) placed upon the charge, will penetrate several sheets of stretched paper, and generally without any appearance of ignition. If a piece of red-hot iron is dropped into the barrel of a pistol, and upon it, powder balls of this kind, they are projected like luminous balls into the air; for, by the combustion of one portion, the remainder is propelled before it has time to take fire. Hence, it appears, that no accurate calculation can be made for the force of ignited powder, nor for the quantity of gas produced by it. Nevertheless, approximate estimations of this kind are well calculated to demonstrate the cause of the effects produced by powder. War powder, according to p. 378, produces theoretically 296 volumes of permanent gas; blasting powder 356 volumes. Suppose the temperature of combustion to be 1200° C. (2160° F.), and the expansion to take place in accordance with known laws, then, at the temperature of 1200° C., war powder would produce 296 $(1 + 0{\cdot}003665 \times 1200) = 1597$ volumes of gas; blasting powder 356 $(1 + 0{\cdot}003665 \times 1200) = 1922$ volumes; in the first moment, when these are compressed into the space of 1 volume, they will exert a pressure of 1597 and 1922 atmospheres, which will, however, rapidly diminish with the decreasing resistance. To project a 12-inch ball 19720 fathoms from a marine mortar, 30 lbs. of powder,—equal to half a cubic foot—will be required; which, according to this calculation, would produce on ignition 798 cubic feet of gas.

Bunsen and Schischkoff give a much higher estimate of the force of gunpowder; for although they find the volume of gas (reduced to the standard pressure and temperature) produced from a given quantity of powder to be much less than that which is assumed in the preceding calculation,—viz., 193 cubic centimetres of gas from 1 gramme of sporting powder (p. 383)—yet,

* To form an idea of the extent of this saving, the cost of blasting must be known; thus, for instance, in erecting water-works at Philadelphia, $12000 or £2512 were expended in powder; in cutting through the Carlton Hill, at Edinburgh, £1256. Even in common granite quarries, a single charge of powder often costs about £4.

on the other hand, they estimate the temperature of the flame considerably higher; and the increase of elastic force thence resulting more than compensates for the smaller volume of gas at a given pressure and temperature.

Direct experiment showed that 0·7125 gramme of powder, burnt in a hermetically sealed vessel, generated a quantity of heat sufficient to raise the temperature of 404·7 grammes of water 1·14° C. Hence the combustion of 1 gramme of the same powder would be capable of heating 643·9 grammes of water by 1 degree. This result, however, requires a small correction for the heat due to the further oxidation of the combustible gases (carbonic oxide, hydrogen, &c.) by the oxygen of the air mechanically enclosed in the powder. From the table on page 383 it is easy to calculate that the 0·7125 gramme powder consumed in the experiment would produce 0·00669 gramme carbonic oxide, 0·00014 gramme hydrogen, and 0·00028 gramme sulphuretted hydrogen. Now the experiments of Favre and Silbermann have shown that 1 gramme of each of these three gases generates by combustion, 2403, 34462, and 2741 heat-units respectively: whence it follows that the quantities above mentioned will together generate 24·4 heat-units; and this, deducted from the total quantity of heat produced in the experiment,—viz., 643·9 heat-units, leaves for the quantity generated by the actual combustion of the ingredients of the powder, 619·5 heat-units.

The temperature of the flame—supposing no heat to be lost by radiation or conduction, is found by dividing this number 619·5 by the specific heat of the products of combustion of the powder, which Bunsen and Schischkoff estimate at 0·207: hence the temperature of the flame is

$$\frac{619{\cdot}5}{0{\cdot}207} = 2993^\circ \text{ C.}$$

If the powder burns in a confined space, so that the gases cannot immediately expand, the temperature of the flame is much higher, being equal to the quotient obtained by dividing the heat of combustion by the specific heat of the products of combustion referred to a constant volume. This latter number is estimated by Bunsen and Schischkoff at 0·18547, so that the temperature of the flame is

$$\frac{619{\cdot}5}{0{\cdot}18547} = 3340^\circ \text{ C.}$$

These numbers must, however, be regarded as theoretical maxima

never actually attained, inasmuch as, when the powder burns in an open space, the temperature of the flame is diminished by radiation and conduction; and when it burns in a space in which the gases cannot immediately expand,—as in the powder-chamber of a heavy gun,—by the sudden expansion of the gases which takes place immediately afterwards.

The pressure which the vapour produced by the explosion of the powder exerts at the first instant on the walls of the powder-chamber and the hinder surface of the projectile, is calculated by Bunsen and Schischkoff as follows: Let G_p be the weight of the powder; S_p its gravimetric density (*i. e.*, the weight of a cubic centimetre of the grained powder); G_r the weight of the residue; S_r the density of this residue at 3,340° C.; v, the volume of gas produced by the combustion, reduced to 0° C. and a pressure of one atmosphere; and t the temperature of the flame: then the pressure P, produced by the powder burning in a space $\frac{G_p}{G_r}$ filled by it, and impervious to heat, is given by the formula—

$$P = \frac{v\,(1 + 0{\cdot}00366\,t)}{\frac{G_p - G_r}{S_p - S_r}}.$$

For the kind of powder used by Bunsen and Schischkoff, the numerical values of these several magnitudes were:—

$G_p = 1{\cdot}000$ grammes.
$S_p = 0{\cdot}964$.
$G_r = 0{\cdot}6806$ grammes.
$S_r = 1{\cdot}50$*
$v = 193{\cdot}1$ cubic centimetres.
$t = 3340°$ C.

Hence, by substitution, the value of p is found to be 4373·6 atmospheres.

If the pressure be calculated on the supposition that the density of the residue of combustion is that which it is found to possess at ordinary temperatures (viz., 2·35), the value of p is found to be 3414·6. Hence it appears that, of the 4,374 atmospheres, about 1000 are due to the expansion of the residue produced by the heat.

The maximum of mechanical effect, or the theoretical working

* The density of the residue was found by experiment to be 2·35 at 18° C. and 1·520 at 2,808° C.: hence, by interpolation, it is 1·50 at 3340° C.

effect of 1 kilogramme of the powder experimented on, is estimated by Bunsen and Schischkoff at 67,419 metre-kilogrammes.*

The results of direct experiments on the mechanical force of gunpowder differ widely from those obtained by the method just described; but they moreover differ so enormously from one another, that very little reliance can be placed upon them. Rumford, in the year 1800, endeavoured to determine the weight with which the mouth of a very massive gun must be closed, in order to prevent the escape of the gases evolved from the powder. This weight would then be in direct proportion to the pressure exerted against the section of the mouth, and would thus furnish a means of ascertaining that pressure. To ensure accuracy, the gun was fired by inserting the barrel into a piece of red-hot iron, which closed at the same time the touch-hole. Nevertheless, great discrepancies resulted. In one case 17 grains of powder, in another $11\frac{1}{2}$ grains were required, to produce a pressure equal to 9431 atmospheres.† When the weight was lifted in these experiments, the effect was always accompanied by a powerful report; when, on the contrary, it was sufficiently heavy to retain the gases in the barrel, on lifting the weight by a lever, a remarkably small quantity of gas escaped with a very slight noise; the products of combustion were found for the greater part condensed on the inner sides of the barrel, in the form of a hard, coaly, difficultly inflammable mass. It is evident, that no accurate results can be expected from this method.

Hutton, from experiments on the velocity of a ball shot from a cannon, estimated the initial force of the powder at 1,700 to 1,800 atmospheres; whereas Van Osten estimated it at 100,000 atmo-

* A metre-kilogramme is the force expended in raising a weight of 1 kilogramme to the height of 1 metre: it is equal to 7·23 foot-pounds.

† An experiment, in which the barrel burst into two pieces, with a charge of $\frac{1}{10}$th of a cubic foot, was used by Rumford as a means of ascertaining the force generated by the powder. He calculated, from the size of the fractured surface, and the known weight which is required to rupture iron wire of a given thickness, that the pressure under which the barrel burst was equal to 412,529 lbs., or 35,000 atmospheres. But the conditions here are quite different from those in dissevering the wire, inasmuch as the air was heated, and very unequally heated, and the bursting of the barrel could hardly take place at all parts at once, but probably proceeded from one part in particular, so that the force was exerted in the manner of a lever, and under much more favourable circumstances than is the case when wire is ruptured. The calculation is therefore probably very much too high.

spheres, and Prechtl's calculations gave a pressure of 14,490 atmospheres for dry powder, and 15,867 atmospheres for powder containing 4 per cent. moisture.

Long experience has, however, established the relative quantities of powder which are necessary, under different circumstances, for producing a given effect, with sufficient accuracy for all practical purposes. These different circumstances are always of the same kind with reference to artillery, where the range is the only thing that varies; whilst in blasting they are very various, loose earth having frequently to be blown up, and at other times, solid rock; sometimes the object is to destroy and hurl the fragments to a distance, and at others to get rid of them in a manner as little dangerous as possible, as for instance, in cases of civil engineering. For the latter purposes, the use of powder has very much increased since the introduction of railroads has given occasion to so many excavations, and since the use of electricity in igniting the charge, has rendered the operation so free from all danger, and removed all chance of failure from the modes of blasting under water. A few examples will serve to illustrate the magnitude of such operations, and bear witness to their successful results.

The line of railroad coming from Folkestone, after passing several viaducts, tunnels, and cuttings, traverses the Abbot's Rock Tunnel. To reach from thence Shakspeare's Cliff (near Dover) in a direct line, the projecting rock at Round Down, an immense mass of chalk, which exactly intercepted the line, had to be removed. The project for removing this rock, which occupied the space of 2400 cubic fathoms, and weighed one million tons, by one single blast, was successfully carried out by Mr. Cubitt. For this purpose, a channel, 36½ fathoms long, was made in the direction of the railroad, and perpendicular to this, three shorter side channels. At the end of each side channel, a perpendicular shaft was sunk to the powder-chambers, each of which was 13·4 feet long, 6·1 feet in height, and 5·5 feet broad. In the chamber towards the east, 5,510 lbs. of powder (50 barrels) were placed, in the middle chamber 7,714 lbs. (70 barrels), and in the west chamber 6,612 lbs. (60 barrels), together, therefore, in the three chambers, 19,836 lbs. of powder. The thickness of the mass of rock from the middle chamber was 85·4 feet; from the two others, 67 feet. At the back of the rock, in a perfectly secure situation, a very powerful galvanic battery was placed under a shed, the covered

copper wires of which, extending 1219 feet over the top of the rock to the chambers below, and always resting on the ground, terminated in very fine platinum points in the middle of the mass of powder. By making connection with the battery, these points were brought to a red heat, and the enormous charge of powder ignited at the same moment. When all was arranged, care was taken to stop up the entrances to the chambers with dry sand. Besides the charge of powder, a considerable quantity of air was enclosed in the chambers. It would have been quite contrary to the desired result to have actually blasted the rock into the air, or hurled the fragments about with a great loss of powder; the only object was to separate the mass of rock, and allow it to roll into the sea. The accuracy with which the necessary quantity of powder had been estimated, was proved by the wonderful success of the experiment. After firing the powder, neither smoke was evolved, nor report heard; no other noise than that occasioned by the tearing asunder of such an immense mass of chalk, was audible to announce the result. The blasted portion of the rock, 500 feet in breadth, began to sink, and slide gradually into the sea, which was distant 36 fathoms. In four or five minutes, all was over. That which was here effected by the force of powder in an instant, would otherwise have taken six months' labour, and have cost nearly £7,500. The circumstances attending the explosion, the absence of smoke and report, prove that the charge was just sufficient to overcome the resistance. The gases evolved had sufficient power to sever the mass of rock, without being able to force a passage for themselves at the moment. The same occurred, therefore, here, as in Rumford's experiments, in which neither smoke nor report was perceptible. In both cases, the volatilized products, and the non-permanent gases, had time to condense, and the other gases to cool, before the walls of the chambers gave way.

The blasting of the Royal George, a ship of the line, is not less interesting. This vessel was sunk whilst repairing, about sixty years ago, in the harbour of Spithead, through the obstinate ignorance of a lieutenant, in water of 90 fathoms; and, as a wreck, rendered the otherwise excellent anchorage unsafe. After some smaller experiments, at first with 198 lbs., and afterwards four successive times with 49½ lbs. of powder, had been partially crowned with success, Colonel Pasley caused, on the 22nd of September, 1839, a cylinder containing 2552 lbs. of powder to

be fixed by the divers to the firmest part of the wreck. From the well-protected cylinder, the conducting wires, covered with a mixture of pitch and tallow, ascended to the surface, and from thence to the galvanic battery, situated in a boat at a distance of 500 feet. Explosions under water are never accompanied by a report, for reasons already mentioned; smoke can still less be produced. This was also the case here: three or four seconds after firing, the water was seen to rise in the form of a bee-hive to the height of 30 feet; it then spread itself out in the form of a sheaf, and lastly, sunk together in numerous muddy rings of waves. On the ships in the neighbourhood a shock was felt, as if from an earthquake. The wreck was, in great part, shivered to pieces. The remaining portion was afterwards removed in the same manner, May 12th, 1840, by the same engineer. On this occasion, the cylinder, with 2328 lbs. of powder, was attached to the keel. The result was similar, but the sheaf of water only rose to half the height, although the shock communicated to the water was greater. When the water had settled down, dead fish and fragments of the wreck were seen floating on the surface; even butter and tallow candles, from the stores of the wreck, were taken up.

Methods of Testing the Force of Powder.

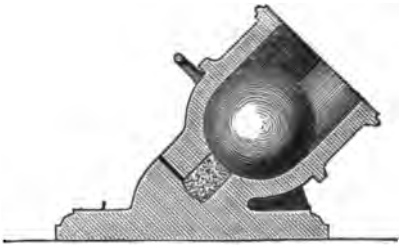
For practical purposes, chiefly connected with military operations, it is necessary to have some ready means of comparing the effects of different kinds of powder with each other. The instruments used for this purpose are called *powder-triers* ("*éprouvettes*"). On firing a charge, not only the ball is set in motion, but also the barrel, and whatever is attached to it. Each time that a cannon is fired, the cannon itself is thrown back several feet, and its motion is slight, only because its mass (weight) is exceedingly large as compared with that of the ball. In the different powder-triers, which, in fact, are only small cannon or mortars, both motions are measured in estimating the force of the powder, viz.: that of the ball, as well as the backward motion of the barrel.

By the method of proof employed in Austria, the height is measured to which a certain weight, inserted between two graduated rods, is raised, on being fired from the mouth of a mortar with a given weight of powder.

With the *testing-mortars* (Fig. 207), on the contrary, the

distance is measured to which a ball of known weight is thrown, when the mortar is inclined at an angle of 45°, and loaded with a certain charge of powder.

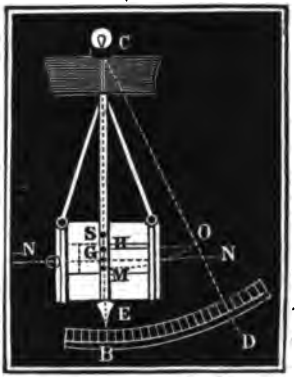
FIG. 207.



The *pendulum-test* differs from these, and can be performed in two ways. The barrel is either suspended as a pendulum, which is then moved by the retro-active impulse, or the ball is fired from a barrel at the side, and lodged in a box containing sand suspended as a pendulum. In both cases, the arc has to be measured, which the pendulum makes on receiving the shock.

The *ballistic pendulum*, or *pendulum of Robins*, consists of a mass, M H, turning about a horizontal axis, C (Fig. 208), which is set into oscillating motion by a ball A projected along N N against it, which serves for the measurement of its velocity. M is its centre of oscillation, the path of which is M O. That as inelastic a blow as possible may ensue, there is an opening made on the further side, which from time to time is filled with fresh wood, clay, &c. The ball remains after each projection sticking in this mass, and oscillating in common with the whole body. For the measurement of the velocity of the ball, it is requisite to know the angle of elongation of this pendulum, on which account there is further a graduated arc, B D, applied, and an index, E, fixed to the centre of gravity of the pendulum, which slides along with the former.*

FIG. 208.



* For extensive series of experiments on both cannon and musket pendulums, and on a great variety of powders, see the "Report of Experiments on Gunpowder, made at Washington Arsenal in 1843 and 1844, by Captain Alfred Mordecai, of the Ordnance Department. Washington, 1845." Eight modes of proof or kinds of éprouvette were used, and in a table at pages

Let M be the weight of the pendulum, m that of the ball, g the height through which a body falls in a second (= 9·808 metres or 32·18 feet), l the length of the pendulum (in metres or in feet), and ϕ the angle of elongation of the pendulum, then the velocity v of the ball is given by the equation :—

$$v = \left(\frac{M}{m} + 1\right) \sqrt{4\,g\,l\,(1 - \cos\phi)}.$$

In France, the powder-chamber is charged with 92 grammes of powder; the shot is a bronze ball 189·5 millimetres in diameter, and weighing 29·4 kilogrammes. All powder that will not carry this ball to a distance of at least 220 metres, is rejected.

The method invented by the Citizen Regnier, in the Year VII. of the Republic, and named after him, applies simultaneously both the backward and forward impulse. A small brass cannon is attached in such a manner to a freely suspended steel spring with two shanks, that it rests with its mouth against the one shank, whilst the back part is connected with the other shank by an iron fork. The one shank on firing, therefore, is moved by the forward

316 to 319, is found a general view of the results, and comparative numerical values of each species of powder. It is there seen that a powder which had a larger proportion of saltpetre than any other of the 60 varieties tried, having in fact the constitution of 77 saltpetre, 13 charcoal, and 10 sulphur, gave the highest average result. Its particles were exceedingly minute. It took 7281 of them to make a grain troy weight. It was highly glazed, and had been incorporated 5 hours in dust barrels, and 4 hours under heavy rollers. Its weight was 1047 ounces per cubic foot or 47 ounces heavier than water. Powder of the same constituents, and in all respects of the same character, except being granulated of the size of coarse cannon powder, of which it took only 9·2 particles to make the weight of a troy grain, gave results in all the modes of proof inferior to those of the fine powder. The average of the eight modes of testing, proved that its relative force, compared with that of the fine powder, was as 867½ to 1000, or it was, by the mere effect of coarse granulation, rendered 13¼ per cent. less effective than if it had been in the finer state of granulation. In another case, cannon powder, of 7·7 particles to the grain troy, gave a force,—compared with the musket powder of the same manufacture, of which it took 113·4 grains to make the same weight,—as 821 to 916. Loss from coarse granulation, 10·3 per cent. In another case, the relative force of powder in particles so fine that 534·9 made a grain troy, was to that of the same powder, so coarse that 11·1 particles only were required to make the same weight, as 959 to 879; loss from coarse granulation—8·2 per cent. In a fourth case, powder of 17·4 particles to the grain, gave a force of 850, and with 1,160 particles, a force of 978—loss 13 per cent. Hence from $\frac{1}{17}$th to $\frac{1}{8}$th of the effective force of powder is lost by too coarse a granulation.—Am. Ed.]

impulse of the ball, whilst the other is affected by the backward tendency of the cannon, and both forces act in such a direction as to cause the two shanks to approach nearer to each other. The amount of this approach, which serves as the measure, can be read off by means of the indicators upon a graduated arc.

The *hydrostatic proof test* is founded on the retrograde action: it is performed by means of a barrel fixed upon a floating support. In consequence of the retrograde impulse, this support is forced down into the water to a certain depth, which is then observed.

Another instrument for measuring the velocity of a ball impelled by a given charge of powder, is the *electro-ballistic pendulum* of M. Martin de Brettes. This instrument consists:—

1. Of a gun-barrel fixed in a frame in such a manner that it can be accurately pointed.

2. Two wooden frames, over which are stretched very fine copper wires about 0·0003 metre in diameter, so as to form continued circuits, the turns of the wire being so close to each other that a bullet cannot pass between them without breaking the wire.

3. Two Ruhmkorff coils, each excited by six Bunsen's elements.

4. The pendulum, properly so called, or registering apparatus, consisting of a small pendulum oscillating in front of a metallic plate covered with paper. The rod of the pendulum extends below the bob, and moves over a divided arc of 0·33 metre radius, carrying at its lower end a point at right angles to the paper, and distant from it by 2 millimetres. The time of a small oscillation is 0·324 of a minute. The metallic plate and the bob of the pendulum communicate respectively with the two poles of the *induced* current of each induction apparatus, so that, at each interruption of the circuit, a spark passes between the point and the metal plate, and pierces the paper, leaving a black mark. At the beginning of an experiment, the pendulum is deflected 75° from its vertical, being retained in that position by a small electro-magnet excited by a 2-pair Bunsen's battery.

To make an experiment, one of the frames above mentioned is set up in front of the gun-barrel, at the distance of 15 metres from the muzzle, and its wire is placed in the inducing circuit of one of the Ruhmkorff's coils. The second frame is placed 10 metres in front of the first, and its wire is connected with the inducing circuit of the other Ruhmkorff's apparatus. The two coils must be placed as near as possible to the respective frames, so as to re-

duce the resistance to the passage of the current as much as possible. The induced current of each coil is carried to the pendulum, placed at the side about 15 metres distant, by two thin, perfectly insulated wires proceeding from the opposite poles. The two wires proceeding from the extremities of the helix of the small electro-magnet, are attached to the capped cock of the gun-barrel, thereby completing the circuit.

The batteries being charged, the circuits closed, the gun loaded, pointed, and capped, and the pendulum raised 75° from the vertical, the trigger of the gun is drawn, so as to depress the cock, break the circuit of the electro-magnet, liberate the pendulum, and at the same time discharge the gun. The ball soon reaches the first frame of wire, passes through it, breaking the wire, and thereby breaking the inducing circuit of the first coil. This interruption excites an induced current in the secondary wire of the first coil, which is communicated to the pendulum, and causes an induction-spark to pass between the point of the pendulum and the metal plate, piercing the paper and leaving a black mark, but neither stopping nor modifying the oscillation of the pendulum. The ball also continuing its course, soon reaches the second frame, pierces it, breaks the wire, and thus produces a second induction spark between the pendulum and the metal plate. The paper is thus pierced and blackened in a second place, and this completes the experiment.

The angle described by the pendulum in passing from the position which it occupied at the instant when the first spark passed, to that which it occupies at the time of passing of the second spark, is traversed in the same interval of time that the bullet takes to pass from one wire frame to the other, the rupture of each wire and the passage of the corresponding spark being exactly simultaneous. Hence the time of describing this arc is the difference of the times $t_2 - t_1$ which elapse between the instant at which the pendulum is released and the moments at which the two sparks pass. These values, t_1, t_2, are obtained either directly, or more quickly by means of a table drawn up for the purpose.

By means of this apparatus, it has been shown that a spherical bullet weighing 27 grammes, impelled by a charge of 10 grammes of powder, [of what quality ?] has, on leaving the mouth of the gun, a velocity of 465 metres per second.

Another electro-ballistic apparatus has been constructed by

Havez, an officer in the Belgian artillery, and has been used extensively in the last four years by the Ordnance Select Committee for determining initial velocities of projectiles, &c. Wheatstone has also recently completed an apparatus for this purpose, which promises to furnish more accurate results than any of the instruments or arrangements hitherto used.

ANALYSIS OF GUNPOWDER.

1. *Determination of Moisture.*—A known weight of the powder is either placed for several days in a vacuum over oil of vitriol, or it is placed in a U-tube kept at a temperature of 60° or 70° C. and exposed to a current of dry air. In either case the loss of weight of the powder gives the quantity of moisture contained in it.

2. *Determination of the Nitre.*—10 grammes of the dry powder are digested in hot water, and the undissolved residue, consisting of sulphur and charcoal, is collected on a small filter previously dried and weighed, then washed, dried, together with the filter, at a moderate heat, and weighed. The total weight, diminished by that of the filter, gives the sum of the weights of the sulphur and carbon, which, deducted from the original weight of the powder, gives the nitre. The latter may also be determined directly by evaporating the aqueous solution, together with the wash-waters, and drying the residue in a small porcelain capsule at 149° C.

3. *Determination of the Sulphur and Charcoal.*—A weighed portion of the dried residue of sulphur and charcoal (or of the powder itself) is digested with a boiling solution of monosulphide of potassium or sodium, or of an alkaline sulphite, which dissolves the sulphur and leaves the charcoal; the latter may then be weighed, after washing and drying, and the amount of sulphur determined by difference.

It is important that the alkaline sulphide or sulphite used in this process be quite free from caustic potash or soda, because, unless the charcoal in the powder consists of pure or nearly pure carbon, the free alkali will act on the organic matter contained in it, producing a peculiar organic acid (ulmic acid) which will then be dissolved, causing the amount of charcoal to come out too small. This precaution is especially important in the analysis of powder made from red charcoal, which contains a considerable quantity of hydrogen and oxygen.

The sulphur and charcoal may likewise be separated by means of bisulphide of carbon. For this purpose, a weighed portion of the dry residue obtained after dissolving out the nitre, is introduced into a small flask, and digested with a mixture of bisulphide of carbon and ether, which dissolves the sulphur and leaves the charcoal. The latter is collected on a small tared filter, washed with the mixture of sulphide of carbon and ether, then dried and weighed. The weight of the sulphur is known by difference; or it may be determined directly by evaporating the solution, and weighing the residue.

The charcoal in gunpowder is not pure carbon, but contains also hydrogen and oxygen, varying in quantity according to the degree to which the carbonization has been carried. Its composition has a great influence on the quality of the powder, and must therefore be determined when a complete analysis is desired. The analysis of the charcoal is made by combustion with oxide of copper.

The quantity of *sulphur* in gunpowder may also be determined by operating directly on the powder itself. For this purpose, 10 grammes of the dry powder are digested in a small quantity of hot water, nitric acid is added, the whole heated to boiling, and chlorate of potash added by small quantities. The sulphur then dissolves in the form of sulphuric acid, and may be precipitated from the filtrate by chloride of barium. The precipitate of sulphate of baryta is collected and washed, with the usual precautions, then dried and weighed, and the amount of sulphur thence determined.

Another method of determining the sulphur, is to mix a known weight of the dry powder with an equal weight of nitre and 4 or 5 times the same weight of chloride of sodium, and throw the mixture by small portions into a red-hot platinum crucible. Deflagration then takes place slowly, without projection of the mixture. When it is ended, the fused mass is taken up with water, the liquid is supersaturated with hydrochloric acid, and the sulphuric acid is precipitated by chloride of barium.

MM. Cloez and Guignet estimate the sulphur in gunpowder by means of permanganate of potash. A weighed quantity of the dried powder is boiled in a small flask with a saturated solution of the permanganate, the boiling being continued, and small portions of the salt added from time to time, till the liquid acquires a permanent purple colour. The whole of the sulphur contained in the powder is thereby converted into sulphuric acid,

and the carbon into carbonic acid, the permanganic acid being reduced to oxide of manganese, which remains suspended in the liquid. Strong hydrochloric acid is then added, and the liquid boiled for a few minutes, till this oxide is completely dissolved. If it is slow in dissolving, the solution is too dilute, in which case it must be concentrated and treated with an additional quantity of hydrochloric acid. Chloride of barium is then to be added in slight excess, to precipitate the sulphuric acid, and the liquid boiled, with addition of a small quantity of nitric acid, to render the precipitated sulphate of baryta heavy and granular; and this precipitate is washed, dried, and ignited, with the usual precautions.

It is sometimes sufficient to determine on the percentage of *nitre* contained in a sample of gunpowder. This is easily done by treating 50 grammes of the powder with 200 grammes of hot water, and filtering the liquid into a glass cylinder having a mark indicating the capacity of 500 cubic centimetres. The residue on the filter is washed with water till the filtered liquid just fills the cylinder up to the mark. The liquid is then cooled to 15° C., and a small quantity of water is added to make up for the contraction caused by cooling. It is then well stirred, to render it homogeneous, and a small hydrometer is immersed in it, graduated in such a manner that the degree to which it is immersed indicates immediately the number of hundredth parts of nitrate of potash contained in the 50 grammes of powder. By this method, the proportion of nitre may be easily estimated within 0·3 per cent. (Regnault.)

STATISTICS.

We cannot pretend to give an accurate statement as to the quantity of gunpowder manufactured or used in this country. We have endeavoured to obtain the quantities consumed in the mines and quarries of Great Britain, and we are much indebted to the following gentlemen, who have kindly answered our inquiries: Messrs. Pease, of Darlington; Liddell, of Newcastle; Hayes, of Runcorn; Gibb, of Aberdeen; Ritchie, of Belfast; Sopwith, of Allcaheads, &c. With their assistance, and information derived from other sources, we have obtained the following results, taking some of the weights of coals, ores, &c., from the

valuable reports of Mr. Robert Hunt, who has also obligingly communicated the other details by letter.

Ores and minerals.			In lbs. per 1000 tons of ore.	Cwt.
Coal	tons	86,039,214 ...	80 =	61,456
Iron ores	„	8,024,205 ...	28 =	2,006
Lead and other ores	„	495,015 ...	7000 =	30,937
Rock-salt	„	121,936 ...	560 =	610
Fire-clay	„	690,665 ...	80 =	493
Granite	„	244,250 ...	650 =	1416
Limestones and sandstones . . .	„	15,764,200 ...	170 =	23,927
		Total cwt.		120,845

This is, of course, exclusive of the quantity used in engineering works for harbours, railways, &c., and that consumed for sporting purposes.

It is also impossible to give the quantity used for naval and military purposes; and we are informed that more gunpowder is consumed by these two branches of the service in times of peace than during war.

The tables of exports do not generally give any details as to the quantity exported, gunpowder being included under the heading of arms and ammunition. Occasionally the quantity of gunpowder is given; thus we have found that the quantity exported was, for the years:—

1854	1	cwt.
1855	11,851	„
1862	145,048	„

The large quantity in the latter year probably arose from the demand created by the civil war in America.

The only other statistics we can find are the following, which relate to France.

French Imports and Exports.

1850.

Imports from England	kilogr.	22,341
„ other countries	„	43
Exports to the West Coast of Africa, United States, Guadaloupe, Senegal, &c.	„	30,653

1855.

Imports from Belgium	kilogr.	15,000
„ other countries	„	30
Exports to the West Coast of Africa	„	18,479
„ Réunion	„	3,840
„ other countries	„	6,456

1859.

Imports from England	kilogr.	20,486
„ other countries	„	277
Exports to Algeria	„	92,900
„ Sardinia	„	22,498
„ other countries	„	61,873

GUN-COTTON.

Pyroxylin; French, *Coton fulminant, Coton-poudre, Poudre-coton, Fulmi-coton;* German, *Schiessbaumwolle, explodirende Baumwolle.*

GUN-COTTON is an explosive substance prepared by treating cotton with a mixture of nitric and sulphuric acids, or of saltpetre and oil of vitriol. It has already found several useful applications in the arts, and promises to be still more extensively employed.

History.—Professor Schönbein, of Basle, towards the close of 1845, announced the discovery of an explosive cotton-wool, which might be used as a substitute for gunpowder. As it ignited with a beautiful flame, and left no residue of ash, this substance attracted much attention, but its inventor kept the mode of its preparation a secret till he had taken out a patent. During this interval however, several chemists had penetrated the mystery; and afterwards gun-cotton was extensively prepared, analysed, and tried for various purposes. It was examined chemically by Otto, Böttger, and Pelouze, Payen, and Peligot, Van Kerckhoff, Sobrero, Béchamp, and others, on the Continent; and in this country by Porrett, Ransom, Walter Crum, and Gladstone. Analyses were furnished by most of these chemists, but the best account of its

chemical composition was given subsequently by Hadow. In the meantime, experiments were performed on its application as an explosive agent, and its manufacture was commenced on a large scale; but several serious and unexplained accidents occurred. In 1847, the gunpowder factory of Hall Brothers, where they were making gun-cotton, blew up, killing every man at work in the place, and the gun-cotton which was left was buried in the earth by the desire of the proprietors. On the 17th of July, 1848, a similar explosion of 1,600 kilogrammes of cotton took place at Bouchet, near Paris. Walls from eighteen inches to a yard in thickness were reduced to powder from top to bottom, and heavy weights were hurled to great distances. An explosion took place in a magazine near Vincennes, which no one had entered for several days previously. These and other accidents threw great obstacles in the way of the manufacture; and at the same time discredit was cast on the application of this material for warlike purposes. Upon the discovery of gun-cotton, the French Minister appointed a commission of inquiry to investigate it. For six years the commission prosecuted its investigations, conducting experiments on a large scale, and instituting inquiries relative to every possible ballistic and other military use to which the material was applicable. Tabulated digests of these results were made; and the record of the experiments may be seen in Berthier's *Mémoire de l'Artillerie*, the verdict being "In the present condition of things, there is no use in continuing the experiments in relation to the employment of gun-cotton in warlike arms." A similar conclusion had been arrived at more speedily by a committee appointed by the German Confederation.

But while the career of gun-cotton, as a destructive agent, appeared thus at an end, an application of it for the healing of wounds was discovered. Gun-cotton, or rather a particular description of it, was found by Domonte and Ménard to be soluble in a mixture of ether and alcohol, and to leave, on evaporation, a transparent tenacious film, impervious to water. This was called COLLODION, and was found to form an admirable artificial skin. Not long afterwards, the same solution was found by Mr. Archer to unite with a solution of iodide of potassium, and to be an excellent vehicle for those compounds, on the decomposition of which by light the photographic art depends.

Yet in one quarter, the value of gun-cotton for military purposes, was still a matter of serious consideration. At an early

period of its history, Liebig had pronounced gun-cotton to be the explosive of the future, and an Austrian artillery-officer, named Lenk, was induced to continue the investigation of the subject. He discovered the causes of the previous failures, and gradually perfected the process of manufacture; and a series of elaborate experiments was instituted by his Government, on the best methods of applying the material to gunnery—while the demolition of the walls of Vienna afforded a good opportunity for testing its powers in another direction. At the present time, thirty-six batteries are arranged in the Austrian service so as to be served with gun-cotton, and it is used in the Imperial quarries near Komorn. But this introduction of gun-cotton has not been achieved without much opposition, an opposition which is still active. A commission of inquiry was appointed under the presidency of Field-Marshal von Fichtenstamm, and this has elicited some valuable reports as regards both scientific and practical points.

The rumour of these proceedings in Austria, naturally attracted the attention of other Governments. The Prussians made similar experiments, with variations, one of which is the employment of little bits of wood instead of cotton. The British Government sent over Major Young to see the Imperial works, and learn whatever the Austrians were willing to communicate.

The British Association for the Advancement of Science also appointed, in 1862, a committee to inquire into the application of gun-cotton to warlike purposes. It was a joint committee from two sections, and consisted of chemists, Dr. Gladstone and Professors W. A. Miller and Frankland; and mechanicians, Messrs. William Fairbairn, Whitworth, James Nasmyth, J. Scott Russell, J. Anderson, and Sir William G. Armstrong. A Report was presented at the Newcastle meeting, August, 1863, and the committee was re-appointed with the addition of Mr. Abel.

To this committee, Mr. Abel, by permission of the Secretary of State for War, communicated the information given by the Austrian Government to the Government of this country, and the results at which he had himself arrived during the course of an elaborate series of experiments.

General von Lenk, by permission of the Emperor of Austria, paid a visit to this country, with the object of answering any inquiries the committee might make, and explaining his system thoroughly; and for this purpose he brought over drawings and

samples from the Imperial factory. It is from this British Association Report, and its Appendix, that the extracts given below are taken.*

Chemical Composition.

Before describing the process of manufacture, it seems desirable to mention some of the chemical characters of gun-cotton, as they will show the necessity of those precautions on which the success of the preparation of Lenk's gun-cotton depends.

By the action of mixed nitric and sulphuric acids on cotton, a number of different substances may be produced. It is the nitric acid which is the efficient body in bringing about the change, and the gun-cotton may be best represented as a substitution-product, in which a different amount of the hydrogen is replaced by peroxide of nitrogen, according to the strength of the acid. These different compounds have different degrees of stability, and are variously affected by solvents. According to Mr. Hadow (*Chem. Soc. Qu. J.*, vii, 201), the three principal products are $C^{36}H^{21}(NO^4)^9O^{30}$, which is insoluble in a mixture of ether and alcohol, but soluble in acetic ether; $C^{36}H^{22}(NO^4)^8O^{30}$, soluble in ether-alcohol and insoluble in glacial acetic acid; and $C^{36}H^{23}(NO^4)^7O^{30}$, soluble in all these liquids. Besides these, there is certainly a much lower compound, to which has been assigned the formula, $C^{24}H^{17}(NO^4)^5O^{20}$, which is soluble in very strong nitric acid, as well as in the organic solvents above mentioned.

The higher compounds are frequently called *Pyroxylin*; the lowest was named by Gladstone *Cotton-xyloidin*, and afterwards by Béchamp *Cellulose trinitrique*. The latter name has given rise to some confusion, for Baron Lenk's gun-cotton, which may be expressed by the formula $C^{12}H^7(NO^4)^3O^{10}$, has been on that account termed *Trinitro-cellulose;* and this seems the origin of a statement which has been officially made, that Baron Lenk's is not the compound in which the largest amount of hydrogen has been replaced by peroxide of nitrogen.

The object of Baron Lenk's process is to effect a perfect con-

* Since this article was written, the British Government has appointed a committee, under the presidency of General Sabine, to make experimental inquiries; the Emperor of the French has also had experiments made. The factory of gun-cotton of Messrs. Prentice, at Stowmarket, has commenced preparing the material on a large scale.

version of the cotton into this highest compound. That such a conversion is pretty well accomplished, is proved by the following analyses of four different specimens, the first of which was made in the laboratory of the Imperial Engineers' Committee, and the others in the University laboratory at Vienna.

	I.	II.	III.	IV.	Calculated.
Carbon	25·1	24·4	24·4	23·9	24·3
Hydrogen	3·0	2·7	2·6	2·4	2·3
Nitrogen and oxygen	71·9	72·9	73·0	73·7	73·4
	100·0	100·0	100·0	100·0	100·0

Process of Manufacture.

The moment cotton is immersed in mixed strong nitric and sulphuric acids, the chemical substitution takes place, and the gun-cotton has only to be freed from the adhering acid by water. But in order to secure the uniform production of the highest product, Baron Lenk adopts several precautions. Of these the most important are—

"1st. The cleansing and perfect desiccation of the cotton, as a preliminary to its immersion in the acids.

2nd. The employment of the strongest acids attainable in commerce.

3rd. The steeping of the cotton in a fresh strong mixture of acids, after its first immersion and partial conversion into gun-cotton.

4th. The continuance of the steeping for forty-eight hours.

5th. The thorough purification of the gun-cotton so produced, from every trace of free acid. This is secured by its being washed in a stream of water for several weeks. Subsequently a weak solution of potash may be used, but this is not essential.

The prolonged continuance of these processes appears at first sight superfluous, but it is really essential; for each cotton-fibre is a long narrow tube, often twisted and even doubled up, and the acid has first to penetrate into the very furthest depths of these tubes, and has afterwards to be soaked out of them. Hence the necessity of time. It seems to have been mainly from want of these precautions, that the gun-cotton experimented on by the French Commission, gave irregular and unsatisfactory results."

The details of the process of manufacture are thus stated by General von Lenk. He has separated under suitable headings the different materials employed, and the different processes.

His description applies strictly speaking to the Imperial Works at Hirtenberg, but it has been in some places altered so as to suit the drawings of the apparatus just erected in this country by the Messrs. Prentice of Stowmarket.

"*a. Cotton.*—Any sort of cotton may be used for the production of gun-cotton, provided it be tolerably free from seed-capsules and oleaginous matter. Absence of the latter is indeed imperative: hence factory cotton, as ordinarily obtained, must be digested in a weak alkaline solution, as is usual in such cases.

Other forms of lignin can be substituted for cotton, to produce an explosive material, viz., flax, hemp, bog-grass, maize, straw, rags, sawdust, &c. I have given rules, so as to meet the case of either of these; however, it is only in some extraordinary cases that any of these materials are to be preferred to cotton. Further, ulterior applications of the explosive material are much facilitated by the device of *spinning* into threads.

b. Nitric Acid.—The nitric acid employed must be in the highest possible degree of concentration; and here the remark should be made, that an impurity of peroxide of nitrogen, imparted to the acid by concentration, which is difficult to eliminate, does not prejudice the acid for this special application.

c. Sulphuric Acid.—The ordinary commercial sulphuric acid, of specific gravity 1·84, answers perfectly.

d. Mixture of the Acids.—This consists of *one part by weight of nitric acid, and three parts of sulphuric acid,* assuming the nitric acid employed to possess an average specific gravity of 1·485. If, however, the specific gravity should differ from the above, then cognizance of the amount of anhydrous acid supplies the data necessary for regulating the mixture."

The mixture is effected by filling one vessel with the predetermined quantity (equivalent to the required weight) of nitric acid, and two others with sulphuric acid. This being done, the acids from the three vessels are allowed to run very slowly into a fourth, in which is an agitator. As soon as a portion of the two acids has been mingled in this manner, the mixture is allowed to run into a reservoir, and the operation is resumed as before.

"The reservoir being completely filled, its contents must be set aside in closed vessels. It is advantageous to preserve the mixed acids a considerable time in the above vessels; in no case must the mixture be used until it has become quite cold.

e. Process of Steeping.—Cotton-wool ordinarily absorbs about

6 per cent. of atmospheric moisture, which must be expelled in a drying-room heated to 95° F. previous to dipping the cotton."

Steeping is effected by the Messrs. Prentice at Stowmarket in an apparatus depicted at Figures 209, 210, 211. The apparatus,

FIG. 209.

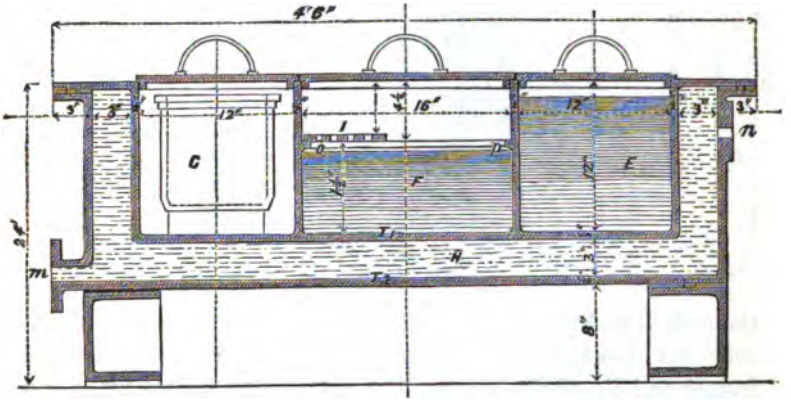
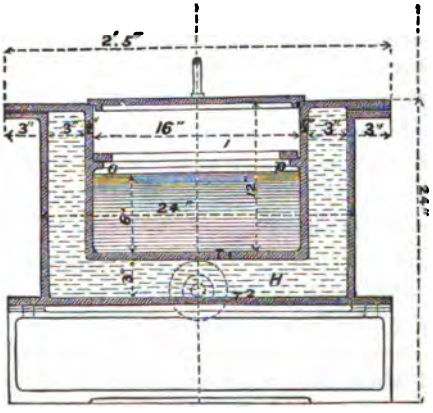
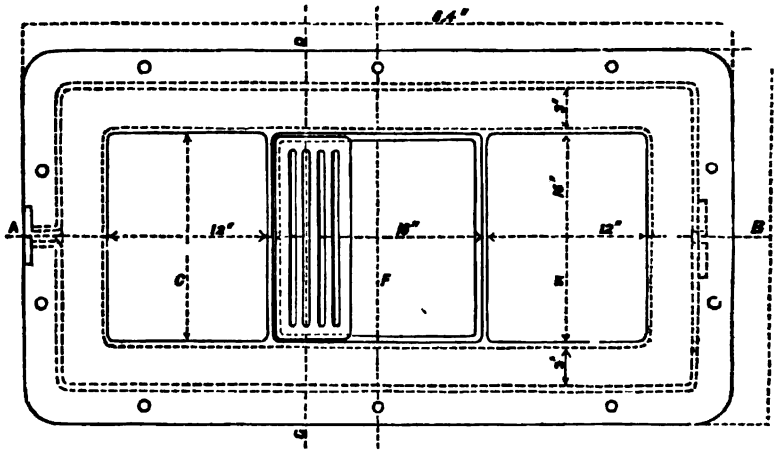


FIG. 210.



during the process, is kept cool by a constant change of cold water poured between the walls T_1 and T_2. E contains 60 lbs. of the acid mixture, G represents the vessel in which the cotton is stored after dipping is accomplished. Two skeins (about 3 ounces) of dried cotton are dipped at one operation, in the mixture contained in E, a spatula being used to effect, by pressure, complete incorporation between acid and cotton; in the next place, the cotton is to be removed from the bath, laid upon

FIG. 211.



the rack I, and pressed to such extent that the amount of mixed acids left absorbed by the cotton, is in the ratio of 10½ lbs. of the former to 1 lb. of the latter. The cotton being now lifted into the vessel G, E is to be refilled, the portion of acid absorbed being made good by means of a tared spoon, in such manner that the surface in E may always maintain the same level for every additional portion of cotton dipped.

The vessel G, filled with the changed cotton and fresh acid, is at length set aside, the due proportion of its contents being regulated. The cotton is next compressed in such manner that it is wholly covered by the acid, to the further action of which it is left exposed for the space of forty-eight hours; it must be cooled during that exposure, thus guarding against the violence of acid reaction resulting in decomposition.

"*f. Removal of Acid from the Gun-Cotton.*—This is performed by means of a centrifugal machine, the drum of which is of copper, a material which lasts a considerable time; after this manipulation, there still remain 3 lbs. of acid in the gun-cotton manufactured from 1 lb. of ordinary cotton. This must be got rid of by rapid water affusion applied in some convenient manner.

Mere affusion, however, does not suffice to get rid of all the adherent acid, hence the cotton must remain for a yet *longer* period in a stream of water, natural or artificial.

g. Impregnation of Gun-Cotton with Soluble Glass.—The object of this process is to close the pores of the gun-cotton fibre by silica precipitated within them, by which the velocity of explo-

sion of the gun-cotton is hereafter retarded; moreover, any lingering traces of acid that may remain are neutralized by combination with soda liberated from the soluble glass. This operation is performed by means of a centrifugal machine, into which a central tube passes for supplying the glass solution. By this arrangement, the liquid is driven in very minute division through the gun-cotton; the glass solution employed has a density of 12° Baumé. The material having been treated as described, has next to be dried by atmospheric exposure; as drying proceeds, decomposition of the soluble glass goes on. Atmospheric carbonic acid uniting with the soda, forms carbonate of soda, whilst silica is precipitated.

The carbonate of soda thus produced, being soluble in water, can be afterwards got rid of by washing, whereas the precipitated silicic acid not being soluble, remains attached to the cotton fibres, protecting them from decomposition under atmospheric influences, however high the temperature may be.

h. Treatment with Soap.—For many purposes, it is desirable to retain the fibres of gun-cotton soft, in order to guard against the contingency of explosion from very violent friction, gun-cotton being somewhat harsh to the touch. This is readily effected by dipping the material, already treated with soluble glass and washed, previous to final drying, into a soap-ley, the excess of which is to be hereafter squeezed out, and the gun-cotton finally dried."

Mr. Abel's account of experiments instituted upon a manufacturing scale at the Royal Gunpowder Works, at Waltham Abbey, will also be found interesting.

"Very considerable difficulties were experienced in procuring the small quantity of cotton (two to three cwts.) required for these experiments, in a condition resembling sufficiently closely that employed at Hirtenberg, as its production in the form of the thick and the thin loose rovings, or yarn, necessitated some deviation from the ordinary method of spinning, which it was difficult to induce manufacturers to attempt without the promise of an extensive order. Eventually I succeeded, through the kind assistance of Mr. Whitworth, in obtaining the requisite quantity of coarse and fine yarn or roving, resembling closely, in character and quality of cotton, the specimens obtained from Hirtenberg, though in the subsequent operations with the coarse or thicker kind no inconsiderable proportion of it was found to be in a much

less compact or more lightly twisted form than the Austrian samples. The comparatively open condition of this portion, and the impossibility of placing it under a sufficient strain to wind it compactly into cartridges, in consequence of the weakness of the yarn, must exert considerable influence upon the rapidity of its combustion in its employment in ordnance (as a few rough experiments at Waltham Abbey have indeed already shown); the gun-cotton prepared from these portions will therefore be carefully separated from the remainder, and will doubtless furnish instructive comparative results in the preliminary artillery experiments to be instituted with the gun-cotton.

The acids of the prescribed specific gravities were readily obtained at moderate prices; the sulphuric acid having a specific gravity of 1·84, and that of the nitric acid (a light amber-coloured acid) being 1·52.

The apparatus and implements employed, and the modes of conducting the various operations, were, as closely as practicable, in accordance with those in use at Hirtenberg; a slight deviation only, in the form or material of some of the implements, being adopted where it was decidedly advantageous and could not in any way influence the nature of the results. The following is an account of the details of manufacture:—

a. Preparation of the Cotton.—The cotton was made up into skeins, those of the stout yarn weighing from four to six ounces each, and those of fine yarn from three to four ounces. It was then boiled for about fifteen minutes in a dilute solution of carbonate of potassa (of specific gravity 1·02, containing one pound of the salt to three gallons of water), and transferred thence to a centrifugal machine, which was maintained for about five minutes at a speed of 500 to 600 revolutions per minute. The alkaline liquid was thus very effectually separated from the cotton, which was then washed thoroughly, first by hand in a large tank, and afterwards by submersion in a stream, for forty-eight hours. At the expiration of that period, the water was separated from the skeins by the aid of the centrifugal machine, and the purified cotton was then dried. Although the cotton was of good quality and very fairly cleaned from seed (being quite equal in these respects to the Austrian samples), it was found to sustain a loss of about 5 per cent. by the treatment with alkali and washing. The potassa-solution in which it was boiled acquired a coffee colour. Portions of seed were still retained by the

purified cotton, which were subsequently dissolved out perfectly by the acids.

b. Preparation of the Acids.—The proportions of acids (three parts by weight, or 2·45 by volume of sulphuric acid to one part of nitric acid) were weighed off and transferred to stoneware barrel-shaped vessels provided with taps, two of these receiving the sulphuric acid and a third the nitric acid. The barrels were so arranged upon a suitable table, that the acids could be delivered from the taps into a deep and very capacious stoneware vessel, fitted with an iron lid with suitable apertures and a tap; this vessel was raised from the ground sufficiently to allow of the acids being transferred from it to well-stoppered stoneware bottles. While the acids were flowing slowly and uniformly from the barrels into the covered mixing vessel, the resulting mixture was kept continuously stirred by means of a large iron paddle, and after they had been entirely transferred (which occupied about ten minutes), the stirring was continued for about twenty minutes before the mixture was drawn off into the bottles. The product of this operation had a specific gravity of 1·82. The elevation of temperature resulting from the mixture of the acids was considerable; in one observation, the temperature of the acids before mixture was found to be 20° C., while that of the mixture, when complete, was 38° C. The acid thus prepared was set aside in a cool place, and never employed until at least twenty-four hours after the mixture had been made.

The mixing process, and all the other operations with the acids, were conducted in the open air, the workmen selecting their positions with reference to the direction of the wind. Thus no injurious effects nor even inconvenience were experienced by those employed.

c. Treatment of the Cotton with the mixed Acids.—About twelve hours before immersion in the acids, the skeins to be operated upon at one time (which had previously been dried in the air) were suspended in a capacious and well ventilated drying-chamber, the temperature of which was maintained, for the above period, at not less than 49° C. They were then transferred, while in the chamber, to stoneware jars with tightly closing lids (the same as were used for keeping the cotton immersed in acid), and were allowed to become perfectly cold in these before submission to treatment with acid.

The vessels which were found most suitable for use in treating

the cotton with the acid, were large and rather deep stoneware pans; one, provided with an iron lid, contained the quantity of mixed acids required for the treatment of a certain number of skeins; a second, which was fitted with a perforated ledge of iron, and surrounded by cold water, served for the treatment of the cotton, which was conducted as follows:—a proportion of the acid having been transferred to the second pan, two skeins were thoroughly immersed in it, and stirred about for two or three minutes; when saturated with acid, they were raised upon the shelf and pressed together with the paddle, so as to allow the superfluous acid to flow off; the quantity of acid absorbed by these skeins was replaced in the pan by an addition of fresh acid, and further skeins were immersed, those which had drained being transferred to a jar while the freshly-immersed ones were soaking. In this way the operation of immersion was continued until the whole of the skeins to be treated at one time had been transferred to the jars; six of the large yarn or nine of the fine being introduced into one of these.

The skeins were pressed down in the jars by means of the paddle, and sufficient acid was added just to cover the cotton completely. The jars were then closed and placed in vessels containing water, in a cool building, where they remained for forty-eight hours.

It was found an important precaution, to keep the vessel in which the cotton was first immersed surrounded with water, especially in the warm season during which these experiments have been conducted, as the evolution of heat during the first action of the acids upon the cotton is considerable. The contents of the jars to which the gun-cotton was transferred, were not found to become heated to any important extent, even when not surrounded by water. The proportion of acid to cotton said to be contained in the jars, as the process is carried out at Hirtenberg, is that of ten to one, but it was found necessary, in order to cover the cotton completely, as directed, to employ at least fifteen parts of acid to one of cotton. This proportion would doubtless be much diminished if means were employed for compressing the cotton in the jars more highly than was the case in these experiments.

The precaution of adding a fresh supply of the acids to that which remains in the immersing vessel after the withdrawal of each quantity of cotton treated, was proved by experiment to be of the greatest importance in securing the uniformity of the pro-

duct. In one of the first operations, no fresh quantity of acid was added before immersing the skeins treated last. In other respects these skeins were submitted to precisely the same treatment as the remainder; *i. e.* an additional quantity of acid was added to them in the jar, they were allowed to remain for forty-eight hours, &c. When examined synthetically, they furnished at least one-half per cent. more cotton than the skeins first treated in the same operation; and when fired in the proof-mortar, a decidedly lower range was obtained with the cotton last treated.

d. Purification of the Gun-cotton.—At the expiration of forty-eight hours, the jars were conveyed to a centrifugal machine, by which the principal quantity of acid was separated from the cotton. The machine employed at Hirtenberg for this purpose is made of copper, the one used by me was constructed entirely of iron, the sides of the revolving cylinder consisting of coarse iron-wire gauze, rendered sufficiently rigid by an iron framework. After each operation, the machine was washed out with an abundant supply of water, and thus the corrosive action of the acids upon it has really been very trifling. The oxide dissolved by the acid when the skeins were placed in the machine, was sufficient to colour the liquid, and also to stain the cotton in places, but these stains disappeared entirely in the first washing which the product received. The skeins were rapidly transferred, by means of an iron hook, to the machine, and the latter was then set in motion, at first slowly, and ultimately at a speed of 800 evolutions per minute. Within ten minutes, the acid was so far separated from the cotton that the skeins were only damp.

Some precautions were necessary in effecting the first transfer to water of the skeins, with acid still clinging to them. If they were simply thrown into water, so that the latter would penetrate them only gradually, the heat resulting from the union of the free acids and the water immediately established a violent action of the nitric acid upon the cotton, quantities of nitrous vapours being disengaged. At Hirtenberg, the gun-cotton, when taken from the machine, is quickly placed under a small cascade, where its saturation with water is effected with very great rapidity. As this arrangement was not attainable at Waltham Abbey, the skeins, directly they were removed from the machine, were plunged singly, as rapidly as possible, and moved about violently, in a large body of water. They were then washed by hand in a stream until no acid taste whatever was perceptible in the cotton, and

were afterwards immersed in the stream for a period of not less than forty-eight hours. For this purpose, they were arranged in rows upon poles fixed in frames, which were so placed in the water that the skeins were in a vertical position, the water circulating among them freely. The current of the stream used at Waltham Abbey (at the only available place for these experiments) was not so rapid as could have been desired, and the dryness of the season had rendered it unusually sluggish; still it was sufficient to afford a continual change of the water surrounding the cotton. The character of this water is by no means such as to render it specially fitted for the purification of the gun-cotton. The bed of the stream is always thickly covered with luxuriant vegetable growth, and the water itself is consequently so highly charged with vegetable matter, that although light was excluded as far as possible from the cotton during its immersion, the skeins became covered in many places, within a few days, by vegetable growth, which in time attached itself so firmly to the cotton, as to be very difficult of removal by hand-washing.

The system of purification, as carried on at Hirtenberg, differs very considerably from that described in General Lenk's process as patented in this country. At the above-named establishment, the gun-cotton is, in the first instance, left in the stream for three weeks and upwards; it is afterwards washed in a dilute solution of carbonate of potash, again washed in water, dried, and then treated with a solution of soluble glass. After this treatment it is dried, washed for six hours in the stream, and finally by hand.

In the patented process, it is directed that the gun-cotton, in the first instance, should be immersed in running water for *forty-eight* hours and upwards; it is not submitted to any treatment with carbonate of potash, but is boiled, after the first washing, in a weak solution of soluble glass, and on its removal from this, without any intermediate desiccation, it is immersed in the stream for about six days.

The process of purification which I adopted, differed from that in use at Hirtenberg only in the postponement of the long-continued washing, until after treatment of the gun-cotton with alkali. At the expiration of forty-eight hours, the skeins were removed from the stream; the water was separated from them in the centrifugal machine; and they were then boiled for a few minutes in a solution of carbonate of potash of specific gravity 1·02. Having been returned to the centrifugal machine, for the separa-

tion of the alkaline liquor, they were again placed in the washing frames, and left in the stream for a period of fourteen to eighteen days. On subsequent removal from the stream, each skein was washed by hand, to separate mechanical impurities, and one-half of each quantity of gun-cotton prepared, was finally left in soak in distilled water for some hours. I found that, in consequence of the very large quantity of salts of lime in the river-water, the proportion of mineral matter in the gun-cotton was notably increased (it varied from 1 to 1·5 per cent.); this final washing was consequently adopted (there being a good supply of distilled water at hand) for the purpose of reducing the proportion of mineral matter added to the gun-cotton by the long-continued immersion in the stream. The gun-cotton thus finally purified, was dried in the open air.

c. "*The treatment of the purified gun-cotton with soluble glass*, which forms one of the features of the Austrian system of manufacture, was stated by the officials at Hirtenberg to effect two important objects, firstly, a retardation of the combustion of the gun-cotton, and, secondly, its protection from atmospheric influences, by the formation of a coating upon the fibres of the cotton. In my account of the results of examination of the specimens of Austrian gun-cotton, I have entered fully into the reasons and facts which lead me to the conclusion that the treatment with soluble glass, the subsequent desiccation, and the final washing of the gun-cotton for five or six hours, do not practically exert any effect upon the properties of the material, the only result being the addition to the mineral constituents of a small proportion of silicate of lime.

"In General Lenk's process, as described in the English patent, the soluble glass is applied, as already stated, to the gun-cotton which, after the removal from the acids, has undergone no further treatment than an immersion in running water for forty-eight hours or thereabouts; when removed from the bath of silicate, the gun-cotton is not dried, but at once immersed for a period of six days in running water. It is at once obvious that this treatment cannot exert any effect upon the cotton, beyond the possible neutralization of a minute trace of free acid still retained by it after the first washing. That the treatment with soluble glass is not intended to exert any other than a purifying effect upon the gun-cotton, appears also to have been understood by Professors Redtenbacher, Schrötter, and Schneider, in their inquiry into

Baron Lenk's system of manufacture; for the only allusion which, in their joint report, they make to this point, is as follows, "the treatment with soluble glass has no influence on Baron Lenk's gun-cotton, it being previously free from acids."

"In order to test, as nearly as possible in its integrity, the system of manufacture as carried on at Hirtenberg, it was determined to submit one-half of each quantity of gun-cotton produced in one operation, to the treatment with soluble glass, the other half being dried, as a finished product, after the immersion in distilled water above mentioned.

"The purified skeins to be treated with silicate of soda were first exposed to air until moderately dry, and then soaked for one hour in a boiling solution of the silicate containing 10 per cent. of that substance. When the excess of the liquid had been subsequently removed by means of the centrifugal machine, the gun-cotton still retained about 80 per cent. of the solution, which, by evaporation, left therefore about 8 per cent. of soluble glass in the material. The skeins were thoroughly dried in air, and then immersed in the stream for about forty-eight hours. A longer period of immersion was adopted than is in use at Hirtenberg, on account of the comparatively sluggish current of the river. The skeins were finally washed by hand and dried, this operation completing the manufacture of the gun-cotton. A comparative examination of the ash of a "silicated" product with that of gun-cotton prepared at the same time, which had not undergone this treatment, exhibited a difference amounting to about one-fourth of the ash existing in the gun-cotton not treated (the latter furnished 1·45 per cent., the silicated left 1·85 per cent. of ash). The proportion of silica left in the gun-cotton was decidedly greater than that found in the Austrian specimens, but the portion not treated with soluble glass also contained a very notable amount of silica, derived from suspended matter in the water. A portion of gun-cotton treated with soluble glass has been washed for a few hours only, for comparative experiment.

"Artificial heat was not employed in drying any portion of the purified gun-cotton. This operation was accomplished by suspending the skeins, during the day, upon lines in the open air, or in a well-ventilated shed in wet weather and at night."

Mr. Abel also states that "several experiments have been instituted for the purpose of examining the characters of the product resulting from the treatment of cotton with the mixed acids which

have already been used once. The quantities of cotton treated at one time, and the various steps in the manufacture, did not differ in any way from those adopted in the regular system in use. The product obtained from the coarse yarn, by means of the once-used acid, has been examined synthetically, and found to correspond very nearly in composition to gun-cotton of the formula

$$C^{36}\left\{\frac{H^{22}}{8NO^4}\right\}O^{30},$$

or the next lowest substitution-product to that obtained in the ordinary process of manufacture. It was found, moreover, that the cotton yarn obtained in this experiment was very decidedly weaker (*i. e.* could sustain only considerably less strain) than the ordinary product,—a result which must be ascribed to the greater predominance of sulphuric acid in the mixture which has been once used.

"Experiments with this mixture and the *finer* yarn, furnished a different result to the foregoing. The products corresponded closely in composition to the theoretical result attained by the original or first employment of the acids. The rotting or weakening effect noticed above was much less apparent in these products than in the case of coarse yarn.

"It would appear from these results that the mechanical condition of the cotton (*i. e.* the thickness of the yarn) exerts an important influence upon the nature of the product furnished by the once-used acid."

Properties of the Gun-cotton so prepared.—This gun-cotton presents to the eye the same appearance as the original fibre, but it may be distinguished under the microscope, as it does not depolarize light.

It is harsher than cotton to the touch. Hence, for some purposes, the Austrian gun-cotton is glazed, so to speak, with a weak solution of soap, to make it softer.

It is insoluble in water, and perfectly unaffected by long soaking in it.

It is not affected by dilute solutions of acids or alkalies. Strong solutions of these powerful re-agents do act upon it. Nitric acid of specific gravity 1·45 attacks it, producing a lower substitution-product, which weighs only $\frac{1}{15}$ths of the original gun-cotton. Strong sulphuric acid dissolves it with some difficulty, and the solution does not turn black, even when heated at a high temperature, though it then gives off carbonic acid and nitric oxide.

A solution of sulph-hydrate of potassium, KS,HS, especially if made with alcohol, reproduces the original cotton, with formation of nitrite of potash, and a little ammonia. Strong potash dissolves it rapidly, especially if the temperature be raised to 160° Fahrenheit, with production of ammonia, nitrous acid, oxalic acid, and other acids. This alkaline solution reduces an ammoniacal salt of silver, and has in fact been used for silvering mirrors.

This gun-cotton usually absorbs 2 per cent. of hygroscopic moisture; and should that quantity be increased through any extraordinary conditions of the air, the gun-cotton speedily parts with its excess of moisture when the air returns to its ordinary state of dryness. It is not liable to explosion by percussion; it may detonate between iron and iron if a heavy blow be struck, but only that part explodes which was hit, without communicating ignition to the surrounding particles. If a heavy blow be struck on gun-cotton with an iron hammer upon bronze or any other comparatively soft metal, or upon stone, no detonation takes place.

There exists some difference of opinion as to the absolute immunity of this compound from slow decomposition; on the one hand, gun-cotton has been stored in Austria, like gunpowder, for twelve years, usually packed in wooden boxes, and no trace of alteration has been discovered; and some that was taken to Italy, during the war of 1859, and thrown aside where it was exposed for years to a hot sun in black boxes, was afterwards found unaltered. On the other hand, it is admitted even by Professors Redtenbacher, Schrötter, and Schneider, that some varieties of gun-cotton, if enclosed together with litmus paper in a tube, often manifest an acid reaction at ordinary temperatures.

Mr. Abel has made the following observations on this point.

"By far the larger proportion of the gun-cotton prepared at Waltham Abbey was dried in the open air, being exposed to strong daylight, and very frequently to powerful sunlight. When dry, it was packed into ammunition-boxes—large wooden cases containing an internal casing of tinned copper and with very tightly closing double lids. In opening some of these boxes containing gun-cotton, a faint but peculiar odour was accidentally observed, which was more distinct in some boxes than others. This observation led to the introduction of some pieces of litmus-paper among the skeins in different boxes, and these were found in some instances to change, after the lapse of time, to rose-colour,

some merely at the edges, others more or less perfectly throughout. The change of colour was like that produced by carbonic acid upon litmus; and if the boxes were left open for some time, the paper gradually regained its original colour. If they were again closed for twenty-four hours or longer, the reaction upon the litmus-paper was again observed in those instances in which it had first been decidedly manifest, but it has been noticed to become gradually weaker. It was subsequently found that the gun-cotton, after it had been for some time exposed to strong daylight, and particularly to sunlight, in the open air, exhibited the same slight acidity, and that the reaction noticed in the boxes was always more marked in those which contained the gun-cotton most recently exposed for drying."

He adds the following account of the gun-cotton which was buried after the explosion at the Works of Messrs. Hall and Sons.

"At my request, Messrs. Hall have been so kind as to have a sample of this gun-cotton, which has been buried for sixteen years, dug up and forwarded to me. This cotton, after being freed from dirt by washing, presented a discoloured appearance, and is stained in many places with oxide of iron, but it exhibits not the slightest evidence of having undergone change. The fibre is perfect throughout, and there is, as might have been anticipated, no trace of acidity manifest in any portion. It is not a rapidly burning gun-cotton, and leaves, upon ignition, a considerable carbonaceous residue; it does not therefore consist, or at any rate not entirely, of the most explosive substitution-product. A specimen, purified in the first instance by treatment with dilute hydrochloric acid, has been examined synthetically, and yielded 59·63 per cent. of cotton,—a result which agrees most closely with that which would be furnished by a product of the composition

$$C^{24}\left\{\begin{matrix}H^{22}\\7NO^{4}\end{matrix}\right\}O^{20}$$

(which would furnish 60·66 per cent. of cotton). Messrs. Hall manufactured the gun-cotton by Schönbein's original process, which consisted, as far as I can learn, in the treatment of the cotton for about one hour with a mixture of one part of nitric acid of specific gravity 1·45 to 1·50, and three parts of sulphuric acid of 1·85 specific gravity. The cotton was washed in running water until no acid was detected by litmus-paper, and afterwards dipped in a very weak solution of carbonate of potassa. The finished

cotton was sometimes soaked in a weak solution of nitrate of potassa.

"The examination of Messrs. Hall's buried gun-cotton appears to afford an interesting and important proof of the permanence of gun-cotton when excluded from air and light, but not protected from moisture, though it is necessary to bear in mind that this particular material does not correspond in composition to the regular Austrian product."

The great value of this gun-cotton depends on its explosive properties. The temperature at which explosion takes place has been very accurately determined by Baron Von Ebner; and in his Report, he fixes the lowest temperature at 136° C. (277° Fahrenheit), but it is stated that it usually requires a greater heat than this. On explosion, gun-cotton is entirely resolved into gases, about 1 per cent. of natural mineral constituents, the small amount of silica, if it has been silicated, and possibly a trace of carbon, being all that is left.

Lieutenant Von Karolyi has fully investigated the products of the combustion of gun-cotton and gunpowder, under circumstances analogous to those which occur in practice.* In his first experiments, conducted in the Laboratory of the Engineer Corps Committee, he exploded the gun-cotton in a Torricellian vacuum, made in a eudiometer, about a metre in length, across which was drawn a very thin platinum wire, that could be ignited by a galvanic battery. The gases were analysed in the usual manner, and the following was the result.

	By volume.	By weight.
Carbonic oxide	28·55	28·92
Carbonic acid	19·11	30·43
Marsh gas	11·17	6·47
Binoxide of nitrogen	8·83	9·59
Nitrogen	8·56	8·71
Carbon	1·85	1·60
Aqueous vapour	21·93	14·28
	100·00	100·00

It was found that by exploding a somewhat larger quantity of gun-cotton under the same circumstances, when therefore the combustion takes place under comparatively greater pressure, the

* Pogg. Annal. May, 1863.

proportional quantities of the products change, and the quantity of binoxide of nitrogen diminishes. Hence the deoxidation of the nitrogen-compounds during the combustion takes place more completely, the greater the work which the gun-cotton has to perform while exploding. This circumstance suggested to Lieutenant Von Karolyi the idea of exposing the gun-cotton during its combustion to a resistance so regulated that it just gives way at the moment when the gun-cotton is completely burnt. He therefore placed a vessel filled with gun-cotton, which offered the necessary resistance, in a sixty-pound mortar, which was then exhausted, and the gun-cotton was exploded by galvanism. A figure of the apparatus is given in the chapter on gunpowder (Fig. 160, page 384). An analysis of the gases produced under these circumstances gave the following numbers.

	By volume.	By weight.
Carbonic oxide	28·95	29·97
Carbonic acid	20·82	33·86
Marsh gas	7·24	4·28
Hydrogen	3·16	0·24
Nitrogen	12·67	13·16
Carbon	1·82	1·62
Aqueous vapour	25·34	16·87
	100·00	100·00

It will be observed that in this latter case, which is analogous to what takes place in practice, no binoxide of nitrogen is formed, but a certain amount of hydrogen, and a larger proportion of nitrogen and aqueous vapour. The importance of this will be afterwards apparent. When exploded in this manner, 10 grammes of gun-cotton was found to yield 57·40 cubic centimetres of gas, at 0°C. and 1 metre pressure. These gases are combustible, on account of the large quantity of carbonic oxide they contain. For the results obtained by Karolyi from gunpowder burnt in a similar manner, see page 385.

Very recently, Mr. Abel has communicated to the Royal Society the results of a series of ingenious experiments on the combustion of gun-cotton and gunpowder. He found that when quantities of gun-cotton, varying from one to two grains, in the form of a loose twist laid double, were ignited by means of a platinum wire in highly rarefied atmospheres, they burned very slowly, presenting

by daylight an appearance as if they smouldered. The pressure in the case described must not exceed 8 inches of mercury; but the rarefaction necessary for the result varies with "the quantity of gun-cotton, its mechanical condition, its position with reference to the source of heat, the quantity of heat applied, and the duration of its application."

The most general statement at which Mr. Abel arrives, is the following:—"Gun-cotton, when ignited in small quantities in rarefied atmospheres, may exhibit, during its combustion, three distinct luminous phenomena. In the most highly rarefied atmospheres, the only indication of combustion is a beautiful green glow, or phosphorescence, which surrounds the extremity of the gun cotton as it is slowly transformed into gases or vapours. When the pressure of the atmosphere is increased to one inch (with the proportion of gun-cotton indicated), a faint yellow flame appears at a short distance from the point of decomposition; and as the pressure is increased, this pale yellow flame increases in size, and eventually appears quite to obliterate the green light. Lastly, when the pressure of the atmosphere and consequent proportion of the oxygen in the confined space is considerable, the cotton burns with the ordinary bright yellow flame. There can be no doubt that this final result is due to the almost instantaneous secondary combustion, in the air supplied, of the inflammable gases evolved by the explosion of the gun-cotton." The pale yellow flame will take place in rarefied nitrogen.

"In a series of experiments made under gradually diminished pressures, oxygen being used instead of air, it was found that the gun-cotton exploded instantaneously, with a bright flash, until the pressure was reduced to 1·2 inch; from this pressure to that of 0·8 inch it still burned with a flash, but not instantaneously; and at pressures below 0·8 inch, it no longer burned with a bright flash, but exhibited the comparatively slow combustion, accompanied by the pale yellow flame." In atmospheres of carbonic acid, carbonic oxide, hydrogen, and coal-gas, this pale yellow flame is seen as in nitrogen; but the two latter gases have a great tendency to extinguish the combustion, doubtless on account of their high cooling powers by convection.

The slow kind of combustion of gun-cotton, in the form of twist, may be obtained also in a powerful current of atmospheric air, if the thread of cotton be placed in a somewhat narrow glass tube. Indeed, it was found that "if, even for the briefest space

of time, the gases resulting from the first action of heat on gun-cotton upon its ignition in open air are impeded from completely enveloping the burning extremity of the gun-cotton twist, their ignition is prevented," and the gun-cotton continues to burn "in the slow and imperfect manner, undergoing a transformation similar in character to destructive distillation." By proper arrangements, these gases may be burnt at the mouth of a tube while the gun-cotton is burning in the interior. There is little doubt that these products of decomposition vary as greatly as the phenomena themselves: "thus, in the instances of the most imperfect metamorphosis of gun-cotton, the products included a considerable proportion of a white vapour, slowly dissolved by water, as also small quantities of nitrous acid, and a very large proportion of nitric oxide;" cyanogen, too, is always found. This contrasts greatly with the simpler products of decomposition found by Karolyi when the gun-cotton was exploded under the pressure of a confined space.

Mr. Abel considers that the remarkable facility with which the combustion of gun-cotton in air or other gases may be modified, might be taken advantage of to produce a variety of mechanical effects; and he states, that by enclosing in suitable cases solid cords made up of two or more strands of gun-cotton, more or less compactly twisted, he has succeeded in producing fuses and slow-matches, the time of burning of which may be accurately regulated.

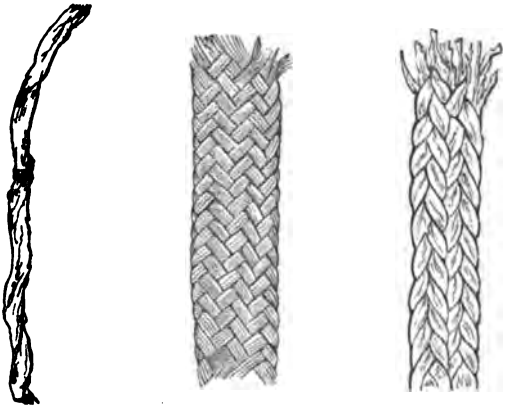
Practical Application to Gunnery.

"Gun-cotton is used for artillery in the form of thread or spun-yarn. In this simple form it will conduct combustion slowly in the open air at a rate of not more than 1 foot per second. This thread is woven into a texture or circular web. These webs are made of various diameters; and it is out of these webs that common rifle cartridges are made, merely by cutting them into the proper lengths, and enclosing them in stiff cylinders of paste-board, which form the cartridge. In this shape its combustion in the open air takes place at a speed of 10 feet per second." The spun-yarn is represented in Fig. 212; two forms of the circular web in Figs. 213 and 214.

"The gun-cotton yarn is used directly to form cartridges for large guns, by being wound round a bobbin, so as to form a spindle like that used in spinning mills. The bobbin is a hollow tube of paper or wood. The object of the wooden rod is to secure

in all cases the necessary length of chamber in the gun required for the most effective explosion."

FIG. 212. FIG. 213. FIG. 214.



The form of these cannon cartridges is shown in Figures 215 and 216.

"Practically, gun-cotton is most effective in guns when used as ¼ to ⅛ weight of powder, and occupying a space of ⅓ths of the length of the powder cartridge, and of such density that 11 lbs. occupy a cubic foot."

In the construction of small-arm cartridges, length is a very important element; and it is requisite to adopt such means as shall ensure their proper explosion by igniting them well in front. Separation of the cotton into several layers by the interposition of paper, has been adopted: indeed, it is said that small-arm cartridges which have answered best, are composed of three layers of flat woven gun-cotton with paper interposed.

When Baron Lenk's gun-cotton is used thus as a substitute for gunpowder, it is found to possess some important advantages, and a few disadvantages. These may be thus stated:

Advantages.—1st. Greater safety during the manufacture. As the material is always immersed in liquid during the process of chemical change and washing, it cannot explode, and the final drying may be performed, if desirable, at the ordinary temperature of the air.

2nd. The possibility of keeping it under water at any time, or of immersing it on a sudden emergency, without damaging it.

FIG. 215.

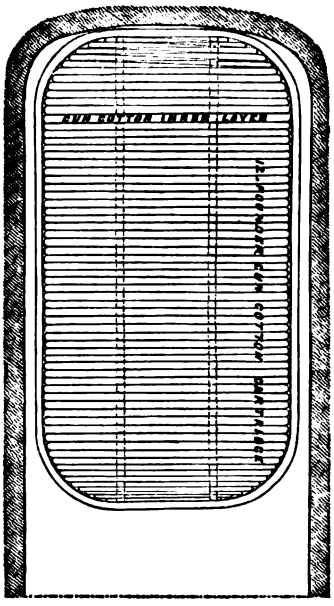
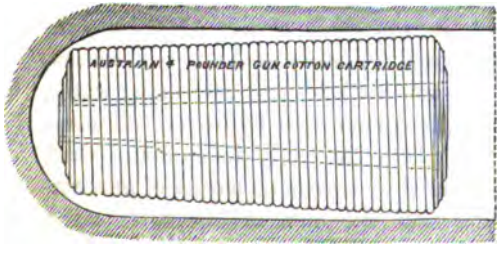
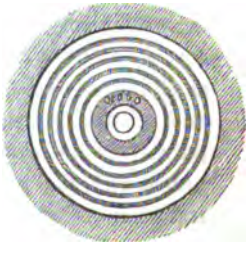


FIG. 216.





3rd. Its being uninjured by damp. "Although gunpowder contains, under normal conditions, less moisture than gun-cotton, it exhibits great tendency to absorb water from a moist atmosphere, which it continues to exert until it actually becomes pasty. Moreover gunpowder, when once damp, cannot be restored to a serviceable condition without being again submitted to the incorporating and subsequent processes."

4th. The conveyance of it is more easy, as one ton of gun-cotton does the work of at least three tons of gunpowder; and it is safer, for there is no fear of the dangerous "getting to dust," and spilling.

5th. The force of its explosion can be regulated so as to produce various results desired. According to its mechanical condition, it may be made to have any speed of explosion, "from 1 foot per second to 1 foot in $\frac{1}{10000}$ of a second, or to instantaneity. The instantaneous explosion of a large quantity of gun-cotton is made use of when it is required to produce destructive effects on the surrounding material. The slow combustion is made use of when it is required to produce manageable power, as in the case of gunnery."

6th. It leaves no residue in the gun on explosion. Hence there is no fouling, and no time lost in sponging out. Hence, also, the windage may be greatly reduced, and the mechanism made more exact, to the great improvement in accuracy of aim.

7th. It produces no smoke Hence the sight of the soldier who is firing is not obscured, nor is his position pointed out to the enemy. Hence, also, more rapid firing is attainable.

8th. The gases produced on explosion are less injurious to the gun, and to the men serving it. Much apprehension was once felt on this subject; indeed it has been stated that both nitrous fumes and prussic acid are among these gases, and that the one would corrode the gun, and the other poison the artillerymen. Now, though it is true that from some kinds of gun-cotton, or by some methods of decomposition, one or both of these gases may be produced, the results of the explosion of the Austrian gun-cotton, without access of air, contain neither of these, but consist, as shown above, of nitrogen, carbonic acid, carbonic oxide, water, and a little hydrogen, and light carburetted hydrogen, all comparatively innocuous gases. "It is distinctly in evidence that, practically, the gun is less injured by repeated charges of gun-cotton than of gunpowder, and that the men in casemates suffer

less from its fumes. The importance of this latter property in a fortress, or a ship, will be at once apparent."

9th. It does not heat the gun so much. "Experiments showed that 100 rounds were fired with a 6-pounder in 34 minutes, and the gun was raised by gun-cotton to only 122° Fahrenheit, whilst 100 rounds with gunpowder took 100 minutes, and raised the temperature to such a degree that water was instantly evaporated. The firing with the gunpowder was therefore discontinued; but the rapid firing with the gun-cotton was continued up to 180 rounds without any inconvenience."

10th. It produces smaller recoil, only two-thirds of that from gunpowder, the projectile effect being equal. This is stated to be a fact, but it is difficult to account for. It depends probably, to a certain extent, on the solid residue of exploded gunpowder having to be projected in addition to the shot, and, as is generally thought, at much higher speed. The remainder General von Lenk attributes to a different law of combustion. On account of the smallness of recoil, a lighter and shorter gun may be employed.

On the other hand, gun-cotton has some disadvantages as compared with gunpowder.

1st. It is suspected of being liable to spontaneous decomposition under certain unknown circumstances.

2nd. It ignites at a lower temperature.

3rd. For use in guns, it requires greater care and precision in the manufacture of the cartridge, lest its great power should be exerted in rending the piece, rather than propelling the ball.

Practical Application to other Military Purposes.

However suitable gun-cotton may seem to be as a source of projectile power, it is still better adapted to other purposes for which an explosive is required. Indeed, its capability of instantaneous explosion enables it to perform easily some descriptions of work, which gunpowder could scarcely, if at all, accomplish.

"The condition necessary to produce instantaneous and complete explosion, is the absolute perfection of closeness of the chamber containing the gun-cotton. The reason of this is, that the first-ignited gases must penetrate the whole mass of the cotton; and this they do, and create complete ignition throughout, only under pressure."

For *fuses*, gun-cotton is woven into a web, steeped in saltpetre,

and covered with an Indian-rubber jacket. The combustion of this takes place at about 30 feet per second, and produces a sharp noise, heating but not tearing the jacket. Such a fuse will fire although a considerable weight be placed upon it, and it may be doubled up without fear of the fire communicating from fold to fold. If ordinary gun-cotton thread be fired, ignition takes place at the rate of only about one foot per second.

Shells with holes are easily filled with gun-cotton web, and projectiles that open may be charged with compressed gun-cotton. In this way a much larger amount of force may be stored up in the shell than with gunpowder, consequently it bursts into double the number of pieces; and it is said that the stronger the shell, the smaller are the fragments into which it is broken. "It is a well-known fact, that a bag of gunpowder nailed on the gates of a city will blow them open. In this case, gun-cotton would fail; a bag of gun-cotton exploded in the same way is powerless. To blow up the gates of a city, a very few pounds of gun-cotton carried in the hand of a single man will be sufficient; only he must know its nature:—in a bag, it is harmless; exploded in a box, it will shatter the gates to atoms."

A small box containing gun-cotton, merely flung down close to palisades, and exploded by a galvanic-battery or a fuse, will open a passage for troops. In an actual experiment on palisades a foot diameter and 8 feet high, driven 3 feet into the ground, backed by a second row of 8 inches diameter, a box of 25 lbs. cut a clean opening 9 feet wide. On this three times the weight of gunpowder produced no effect whatever, except to blacken the piles. When several of these boxes were placed at short intervals against a palisade and ignited by fuses, it was found that only one or two of them had produced any effect; the truth was, that the box which first exploded blew its neighbours away. When they were ignited simultaneously by galvanism, the whole number took effect on the piles.

The same force has been applied to the destruction of bridges. "A strong bridge of oak, 12 inches scantling, 24 feet span, was shattered to atoms by a small box of 25 lbs. laid on its centre: the bridge was not broken, it was shivered."

For military mining, the gun-cotton charge is placed in little barrels with strong hoops.

The effect of gun-cotton when exploded under water, is very remarkable. The action is so instantaneous that the water has no

time to yield, and thus it is unnecessary to place the charge in contact with the body to be destroyed, as is said to be the case when gunpowder is used. Two tiers of piles, 10 inches thick, in water 13 feet deep, with stones between them, were blown up by a barrel of 100 lbs. of gun-cotton placed 3 feet from the face and 8 feet under water. It made a clean sweep through a radius of 15 feet, and raised the water 200 feet. The iron anchor used to keep the box in position, was found broken across. At the close of the Italian campaign, some experiments on ships were made at Venice, in the presence of the Emperor of Austria. In one of these, a barrel of 400 lbs. weight was placed near a sloop in 10 feet of water, the nearest part of the hull of the vessel being about 18 feet distant; yet the sloop was broken to pieces, and these were hurled into the air to the height of 400 feet. This kind of explosion is attended with terrific noise. It was observed that the fishes, for perhaps half a mile round, were stunned, and floated on the surface. They recovered after awhile, but not till many had been picked up by hand.

Application to Blasting.

"Gun-cotton thread is spun into ropes in the usual way, up to 2 inches diameter, hollow in the centre. This is the form used for blasting and mining purposes; it combines great density with speedy explosion, and in this form it is conveniently coiled in casks and stowed in boxes. The fact that the action of gun-cotton is violent and rapid in exact proportion to the resistance it encounters, tells us the secret of its far higher efficacy in mining than gunpowder. The stronger the rock, the less gun-cotton, comparatively with gunpowder, is necessary for the effect; so much so, that while gun-cotton is stronger than powder as 3 to 1 in artillery, it is stronger in the proportion of 6·274 to 1 in a strong and solid rock, weight for weight. Its power of splitting up the material, can be regulated at will." As it is not liable to be spilt about by the miners like powder, there is less danger of accidental explosion. The absence of smoke in its explosion, also, conduces to the comfort of the workmen.

COLLODION.

Nature of the Gun-cotton used.—It has already been stated that the highest nitro-substitution product of cotton, that is, the one we have hitherto been describing, $C^{36}H^{21}(9NO^4)O^{30}$, does not

dissolve in a mixture of ether and alcohol, but that the lower compounds are capable of doing so. It is these compounds, therefore, which are alone available for making that solution of gun-cotton which is known by the name of collodion. They are produced when weaker acids are employed, or when the precautions mentioned above in the preparation of Lenk's gun-cotton, are not observed. As they are not prepared in a state of chemical purity for the manufacture of collodion, it would be out of place to describe them fully here; but the following properties may be noted.

They do not resemble the original cotton in appearance so closely as the highest compound does; for they show more signs of the action of the acid on the fibre. Indeed, there is at least one compound which is soluble in nitric acid, whether fuming, or of as low a specific gravity as 1·25, and may be precipitated as a granular powder on the addition of water.

They explode at a lower temperature, but this temperature depends both upon the nature of the compound and the manner in which the heat is applied. A long-continued heat will explode a mass of such gun-cotton which at first was not set on fire; and there can be little doubt that, under such circumstances, it may be exploded at a temperature very little exceeding that of boiling water; indeed much lower temperatures have been mentioned by some observers.

When exploded, these lower compounds leave a certain amount of carbonaceous residue.

All these substitution-products dissolve in strong sulphuric acid, but a solution of cotton-xyloidin in that acid is charred at as low a temperature as 180° Fahrenheit.

These lower compounds are liable to spontaneous decomposition. This takes place very slowly at first, but when it has reached a certain point, perhaps after the lapse of several years, the action becomes much more rapid. It does not appear to be proved that any gun-cotton ever *explodes* without extraneous heat. Light certainly favours this decomposition, but is not indispensable, for it is on record, that gun-cotton stowed away in casks has evolved a choking smell after some months. The usual progress of decomposition is of this character:—the gun-cotton begins to emit a peculiar odour, rather agreeable than otherwise; the gas increases, perhaps driving out the stopper, if the gun-cotton be contained in a stoppered bottle; the cotton becomes damp, and shrinks together; and, as decomposition goes on, the fibre disappears,

and there remains a gummy mass, probably interspersed with crystals. The gases include nitric oxide, and apparently, in some cases, prussic acid; the crystals are oxalic acid, and the residue is a mixture of products, consisting of water, nitric acid, and several organic acids, not always soluble in water.

Preparation of Collodion for Photographic Purposes.

The fullest and best description of the preparation of collodion is that given in Mr. T. F. Hardwich's Manual of Photographic Chemistry. The following is his account of the process, the subject being naturally divided into the preparation of the pyroxylin (or gun-cotton) itself, and its solution in a mixture of ether and alcohol.

"*The Nitre Process.*—Use only the best nitre; and having reduced it to powder, dry on a hot metal plate, or in an oven heated to a temperature above that of boiling water. Then pulverize a second time, to prevent the formation of lumps on adding the oil of vitriol. Take of

Oil of vitriol	6 fluid ounces.
Dried nitre	3½ ounces (avoirdupois).
Water	1 fluid ounce.
Best cotton wool	60 grains.

"Mix the acid and water in a tea-cup, or any porcelain or stoneware vessel, and throw in the pulverized nitre by degrees, stirring meanwhile with a glass rod, until lumps have disappeared, and a transparent, viscid liquid is obtained.

"Pull out the cotton into separate balls of the size of a walnut; and when a thermometer dipped in the acid, and stirred backwards and forwards, remains stationary at 140° F., immerse the lumps singly with a glass rod, and press each against the side of the cup. This part of the operation ought not to take more than two minutes. Supposing the acid to have cooled down below 140° during the pulling out of the cotton, float the cup upon boiling water for a few minutes until the exact temperature is attained. Leave the cotton in for ten minutes, and afterwards pour off the excess of the acids, and squeeze the pyroxylin with the glass rod. Do this quickly, and then dash the cup and its contents suddenly into cold water, as presently to be advised.

"*The Process with Mixed Acids.*—Larger quantities may be operated on in this case, as the chances of alteration of temperature are diminished thereby. Take of

Nitric acid, specific gravity	1·45	6 fluid ounces.
Oil of vitriol „	1·84	18 „
Water		4½ „
Cotton		400 grains.

"Procure a porcelain vessel of some depth, and exposing only a small surface to the air. Put in first the water, then the nitric acid, and lastly the sulphuric acid. Next agitate for two or three minutes with a glass rod, until the acids have thoroughly mixed. This is important.

"A thermometer dipped in the mixture will probably indicate 165° or 170° F., but in the course of ten or twenty minutes, the acids will cool down to 140°, which is the proper temperature for immersing the cotton.

"As the exact temperature is of great consequence, the following directions must be observed:—Stir the acids with the thermometer, and move the bulb several times up and down before reading off the height of the mercury. Also, place the vessel upon a badly conducting material, such as a block of wood, or the same covered with flannel, since stone or metal would cool the lower stratum of the mixture, and alter the temperature some five or six degrees.

"The cotton-wool must be of the finest quality, well bleached, and carefully combed from brown specks. First divide the 400 grains into two equal weights, and then pull out each portion into about twenty separate tufts, which are to be immersed singly when the acids have cooled to the proper point. A thick glass spatula may conveniently be used to press the cotton against the sides of the vessel, and expel bubbles of air, or in place of it, three or four stout rods bound together at the upper part with string. Work the cotton well about, in order to ensure it taking the acids; but let no time be wasted, since, if more than three or four minutes elapse, the first portions will undergo some solution, and the last will be immersed at a variable temperature.

"Cover the vessel and leave it *exactly ten minutes.* The process is complete in half that time, but the extra five minutes, although producing a little more solution of the pyroxylin, and consequently diminishing the weight of the product by about 15 per cent., produces a collodion less likely to show glutinous markings upon the glass, or to dry up speedily and repel the developer.

"The removal of the cotton from the acids must be done quickly. Lift it out, if possible, in one mass, and squeeze it with the rods against the sides of a large shallow capsule; in about one minute,

pour back into the deep porcelain vessel as much of the acid as will flow away, and dash the capsule, with its contents, into a large quantity of cold water; then, without one moment's delay, seize the ball of pyroxylin with the hand, and move it about rapidly, until it ceases to feel warm, and is dispersed in separate pieces throughout the liquid.

"If any failure occurs at this part of the process, it will probably be from the pyroxylin decomposing suddenly, with evolution of red fumes, which the writer has known to happen at very high temperatures when the acids were pressed out leisurely, and the pyroxylin left in the capsule exposed to the air; or secondly, a failure might arise from afterwards throwing the ball of pyroxylin into a small quantity of water, and not moving it about sufficiently, in which case the temperature starts up, and the cotton is disintegrated. Another point, however, worthy of note, although not of equal importance with the last, is that the cotton must not be allowed to rise to the surface of the acids during its digestion; otherwise the pyroxylin, on coming into contact with the air, will often decompose and evolve red fumes, as before mentioned.

"Having made one half of the cotton into pyroxylin, warm up the acids again in a hot-air bath to 144°, and add six drachms of oil of vitriol, to combine with the water extracted from the cotton, and restore the mixture to its original strength; then allow to cool to 140°, and put in the second portion of the cotton weighing 200 grains, with the same precautions as before. After taking out this second quantity, the acids may be thrown away.

"Directions for Washing.—Pour off the first water quite close, and afterwards keep a tap running over the vessel for forty-eight hours. A very much shorter washing would suffice to remove all the acid, excepting a mere trace; but when time is not an object, it is better to use the full quantity of water.

"The washing being complete, wring the pyroxylin, and having well teased it out, dry it by exposure to the air on sheets of blotting paper. In the summer it may be finished by the heat of the sun, and in winter over oil of vitriol in a drying-dish. Artificial heat is not very safe.

"*The plain Collodion.*—Take of

Dried pyroxylin	. . . . .	500	grains.
Ether, specific gravity, 0·728	.	36	ounces.
Alcohol „ 0·816	.	12	„
Alcohol „ 0·800	.	6	„

"If the whole of the alcohol employed be absolute, there will not be quite enough water in the collodion to dissolve the whole quantity of iodide of potassium, and therefore the composition of the iodizer must be a little modified, as advised in the next section. On the other hand, if no absolute alcohol be used, but the whole of the spirit be that at 0·816, the iodized collodion will sometimes be slightly ropy towards the bottom of the bottle.

"Put in the pyroxylin and shake the bottle for five or ten minutes, until the transparent jelly-like masses which adhere to the bottom have dissolved. Then drop in a strip of blue litmus paper, and leave the collodion for twelve hours to settle. At the end of that time the paper should still be blue.

"*Collodion for the Dry Process.*—In this case the same formula as before is employed for the nitro-sulphuric acid, but the cotton is immersed at a higher temperature, viz. 160° to 165°. A considerable amount of solution takes place, and the dry product weighs less than the original cotton. The pyroxylin is short and powdery in appearance, and dissolves in the ether with a residue, like the ordinary kind.

"To make the plain collodion, take of

Soluble pyroxylin	600 grains.
Pure ether, 0·728	35 ounces.
Alcohol . 0·800	25 ounces.

"This alcohol is stronger than that recommended for the ordinary negative collodion; the object being, to use as much of it as possible, in order to diminish the contractility of film and tendency to peel away on drying."

It is well known that if woody fibre, such as paper, be steeped in sulphuric acid diluted with half its bulk of water, and afterwards well washed, its properties are changed, and it becomes "parchmentized." Such fibre is more soluble in ether and alcohol. Collodion prepared from it, is found by Mr. Hardwich to have an increased fluidity and freedom from structural lines; and after development, the film appears unusually tough and contractile. "To secure the full parchmentizing action in the ordinary process of making pyroxylin, the amount of sulphuric acid present should be considerably greater than that of the nitric acid. The physical modifications produced by sulphuric acid are seen in an exaggerated degree when the nitro-sulphuric mixture is heated before putting in the cotton. An acid which gives an insoluble and explosive product in the cold, will yield pyroxylin perfectly soluble

at a higher temperature." Good photographic pyroxylin may be made at a temperature even as high as 200° Fahrenheit; but in this case the quantity of water in the acids must be reduced to a minimum, or immediate solution of the cotton will take place.

Other substances than cotton-wool may be used for preparing collodion. Mr. Hardwich states that calico is more liable to be dissolved by nitric acid than the original cotton, and is more likely to give rise to a bitter resin which diminishes the sensitiveness of the film to obscure rays. Linen yields a more limpid collodion than calico, and gives a less tenacious and contractile film. Old rags are said to be quickly disintegrated by the acid mixture, "and produce a highly structureless collodion, which adheres with much tenacity to the glass." Paper is not approved of, even in the form of the Swedish filtering paper.

Thus far the directions and opinions of Mr. Hardwich have been quoted; but upon the best methods of preparing collodion there is a considerable difference of opinion among those who have practically studied the subject. Mr. Charles Heisch uses the following ingredients and proportions:

Nitrous acid, as free from chlorine as possible, specific gravity, 1·430	39 oz.
Sulphuric acid, monohydrated	31 oz.
Swedish filter paper, cut in pieces 1 inch square	10 sheets.

The paper is to be immersed when the acid is at about 130° Fahrenheit, at which temperature it should be kept for about an hour. The product should be well washed after pouring off the acid, and finally treated with a little very dilute ammonia, again washed and dried. This may be dissolved in equal parts of anhydrous alcohol and ether. Alcohol not quite so strong, makes rather more sensitive collodion, but the film is not so strong or structureless. In making large quantities of pyroxylin, he finds it better to allow the acid to cool to 125° F. before putting in the paper.

Other Applications of Collodion.

Collodion has been employed in surgery, to form an air-tight covering for wounds and burns. For this purpose it is made as contractile as possible.

Heisch recommends the use of nitrous acid, of specific gravity 1·45, and a lower temperature than 130° Fahrenheit, to prepare the pyroxylin for this purpose, ten or twelve grains of which may be dissolved in an ounce of a solvent consisting of one part of

alcohol and three of ether. To render the film more elastic, a little castor oil is sometimes added, and it has been recommended to mix seventy parts of collodion with one of turpentine, one of castor oil, and one of white wax dissolved in three of ether.

Collodion has also been used as an envelope for caustic substances and for pills. Fabrics may be rendered waterproof by means of it.

Another application is, for making balloons lighter than those of gold-beaters' skin. For this purpose, a thin solution of collodion is poured into a glass flask, which is turned about, to spread the liquid uniformly over it, and then inverted, so as to allow the excess to run out. The ether is evaporated by blowing into the flask with a pair of bellows, by which the collodion is left as a thin membrane on the surface of the glass. To remove it, the edges of the film are loosened from the glass, a glass tube is inserted into the neck of the flask, the balloon is made to adhere to it, and the air is slowly drawn out with the mouth. The balloon then detaches itself from the vessel, contracts, and is easily withdrawn through the neck. It must be immediately blown out and tied at the neck, so that it may dry distended. Large balloons are apt to contract very much in drying, which, however, may be prevented by performing the process in warm air. They may be made so thin, that a balloon, with a capacity of a hundred cubic centimetres, shall weigh only 0·03 gramme. These balloons become strongly electric by slight friction, but their principal use is in lecture rooms, for the explosion of detonating gas, which easily raises them into the air, and on ignition balloon and gas both disappear.

MECHANICAL APPLICATIONS OF GUN-COTTON.

The uses to which we apply explosive compounds, such as gunpowder, fulminating mercury, and gun-cotton, are chiefly of two kinds, the first of which we may term "destructive effect," and the second "mechanical duty."

First, we turn the *destructive effect* to practical use when we apply it to remove obstacles out of our way or to destroy the cohesive forces of resisting materials: in short, to destroy the strength of materials. The collier brings down a mass of coal

from the solid stratum, by a gentle explosion, which merely detaches the mass of coal, without crumbling it into powder. The quarryman detaches a mass of granite from the solid rock, by a series of small charges placed in a straight line, forming the boundary of the mass which he wishes to bring up. The commander of an army directs a charge of gunpowder to be nailed on the gates of a fortress, and its sudden explosion destroys the gate; or he undermines the fortification, and filling a large subterranean chamber with gunpowder, removes, by a single explosion, a sufficiently large portion of the ramparts to make a wide and practicable breach for the entrance of the storming party. A retiring army places a mass of gunpowder on or under the arch of a bridge, so that its explosion may delay pursuit. A threatened harbour is protected by a mass of gunpowder floating under the surface in the centre of a channel, so that no ship can pass without striking the obstacle and having the submarine mine exploded under its bottom. Such are some of the destructive agencies in which explosives are employed.

It is plain that in such applications we need care little about the way in which this destruction is accomplished, provided only the destruction be complete: whether the materials so destroyed are destroyed by an instantaneous action through a short space, or a milder effort during a longer time, is a matter of comparatively little consequence. The miner has only to see that he wastes no powder; and he soon learns to put in no more than will just do his work without waste. If, however, he used an explosive mixture which would shatter the coal into dust, that would be waste of the worst kind, and such explosives would be useless to him. If the quarryman wants a large block detached in a single piece, he must take care that the force he employs does not crack the block as well as bring it away; but when the stuff which is burst asunder is merely to be destroyed, it matters nothing whether it is exploded into dust or blown away in large fragments.

Mechanical Duty.—It is only when we come to the skilled use of explosives, that we require to study with great care the nature of the work to be done, in order to apply the force in such a manner that it shall accomplish the one thing intended, and no other. Mechanical duty is the well-known phrase used with reference to the steam-engine, when we employ it to perform a measured quantity of mechanical work. Sometimes that work

is a certain number of pounds weight of water taken from a mine and brought to the surface. Thirty-three pounds of water raised from a mine 1000 feet deep forms the usual measure of one horse power, or, as we sometimes call it, 33,000 foot-pounds. Sometimes it is a ship pushed through the water 1000 feet against a resistance of water of 33 lbs., and that also is one horse power or 33,000 foot-pounds. Sometimes it is a train of goods dragged up an inclined plane on a railway; and there also we multiply together the number of pounds force employed, and the number of feet over which it is employed, and divide the product by 33,000 to find the number of horses' power exerted. In reducing it to horses' power, we have to remember that this is what a horse can do every minute for eight hours a day—at least a steam-horse can do this. When, therefore, we consider the mechanical duty performed by explosive compounds, we have to compare that duty with that of steam, air, water, and other mechanical agents. We have to ascertain the nature of the duty: we have to measure the amount of the duty; and we have to consider the manner in which that duty can be performed most economically, most efficaciously, and most rapidly; and we have in every case to remember that the duty of these compounds, and their value for the intended purposes, must be ultimately measured by the number of foot-pounds which they perform, by the time of that performance, and by the quantity of material required to perform it.

On the Nature of the Mechanical Duty to be performed in Artillery.—The projectile duty to be done by an explosive power in the barrel of a gun, bears a close resemblance to that done by steam in the cylinder of a steam-engine. The barrel of the gun, like the cylinder of the steam-engine, is a strong, long tube, bored perfectly true and cylindrical, the inside of which is filled more or less exactly by a smooth plug, generally of iron, which is brought down near to the bottom of the cylinder or barrel, which has the steam or gunpowder placed in the cylinder immediately below the piston, the duty of the steam or gunpowder being to raise that piston from the bottom of the cylinder to the top. Thus far the cases are alike, the difference being that the piston is allowed to leave the barrel with its acquired speed in the case of artillery, while it is stopped, and used over again in the case of the steam-engine. Every discharge of the barrel requires a new piston in the one case, but it is repeated by the old one in

the other over and over again. Steam and gunpowder are therefore alike in the mode of their application to the performance of mechanical duty: it is not at all wonderful, therefore, that steam should have been employed for guns, and gunpowder employed for engines. A gunpowder engine is an old invention, and steam guns are a modern invention; but each hitherto has been more successful in its own proper application than in the other. It is an interesting inquiry whether steam will not supersede gunpowder, or that gun-cotton may not supersede both in some of their applications.

1. *The Mechanical Duty of a Gun.*—The mechanical duty of a gun is to carry its piston or projectile from the breech of the gun to the muzzle, and to deliver it at the muzzle with a required velocity. This required velocity is technically called "initial speed." The "initial speed" ought perhaps to be called the "final speed," in our present inquiry, because it is the speed which the projectile acquires at the end of its course through the gun; and the work is, to start the projectile from a state of rest at the breech, to accelerate its speed gradually, and to deliver it finally out of the gun, either with the highest possible velocity, or with that velocity which is wanted for the purpose in view. In relation, therefore, to the exploded charge which propels it, and to the mechanical duty done in the gun, it is the "final velocity;" but with regard to the artillerist, it is the "initial velocity," because it is the velocity with which the missile commences its flight in the air. And this initial velocity is being continually diminished by the resistance it meets with in the air, until it terminates its flight by encountering an obstacle, which ultimately brings it back to rest. In this way it will be seen that the flight of a projectile consists of two quantities of work done:—first, a quantity of work put into it by the explosive charge, while it is in the barrel of the gun; and, secondly, the same quantity of work taken out of it by the resistance of the air, or by the resistance of the obstacle which it finally strikes. But it is to be observed that the projectile is a mere vehicle of power; the mechanical power put into it by the gunpowder, it carries with it to the end of its flight, and delivers it to the obstacle it encounters, deducting only such of its power as it has communicated to the air in its passage. It is with the second half of its history that the artillerist has mainly to do in the use of his gun; but it is with the first part of its history, while it flies from the breech to

the muzzle of the gun, that we have to deal in measuring the duty of explosive compounds.

To examine this further, we will take a single gun—the well-known piece called the 68-pounder—a gun 8 inches in diameter, with room enough in its chamber for a charge of 16 lbs. of powder, and length of barrel beyond it enough to contain a round shot weighing 64 lbs., and to allow that shot to travel 8 feet before being dismissed into the air. The work to be done, then, is to carry a ball weighing 64 lbs. along a cylinder 96 inches long, and in that short space to put into it so much power as to deliver it from the muzzle with a speed of 1600 feet per second. That is the duty of this well-known piece—the great naval gun.

2. *How to do this Work.*—The difficulty of doing this work consists mainly in the shortness of the time in which it has to be done: 1600 feet in a second, would allow only the 200th part of a second for passing over 8 feet, and if we conceive double that time to be allowed for the gradual acceleration of the speed, it leaves but the $\frac{1}{100}$th part of a second for the whole time of the passage of the shot from the breech to the muzzle, or for doing the whole work of the explosive charge. We have, therefore, to consider how the work is to be done in the $\frac{1}{100}$th part of a second, and how the force can be applied in order to do it. For this purpose we will divide the $\frac{1}{100}$th part of a second into ten equal parts, and call them *instants*. Let us conceive, now, that we can apply to the shot a uniform measured pressure, like that of steam, or any other uniform measured power of a given force upon each round inch of the piston or barrel: let us take a force of 5000 lbs. pressure per round inch, and let us suppose this force of 5000 lbs. to press on the projectile: this force will be sufficient to move it forward through one inch in the first $\frac{1}{1000}$th part of a second: continuously applied, it will force the piston through 3 inches in the second instant: through 5 inches in the third: through 7 inches in the fourth, &c. in the following manner, viz.:—

Instants . .	1	2	3	4	5	6	7	8	9	10
Spaces . .	1	3	5	7	9	11	13	15	17	19

If we now add together all these inches, we shall find that the ball has passed through 100 inches in $\frac{1}{1000}$ths of a second, and we know that it will have, at the end of that time, a speed which would carry it over double that space, or 200 inches in the next $\frac{1}{100}$th of a second. As 200 inches is a little more than 16

feet, we know that we have a velocity exceeding 16 feet per $\frac{1}{100}$th of a second, or 1600 feet per second. Here then we have the full measure of the power required, or the full measure of the work to be done, viz. :—

$$\frac{\text{5000 lbs.} \times \text{8 feet}}{\frac{1}{100}\text{th part of a second}}.$$

It is plain now, therefore, that in order to do this work as we have marked it out, the explosive charge must supply enough force to follow the shot through one inch of the barrel with a propelling power of 5000 lbs. during $\frac{1}{1000}$th part of a second. It must supply 3 inches with the same quantity of pressure in the next instant; 5 inches in the third instant; 7 inches in the fourth instant, and so on: in other words, the quantity of propelling power must increase uniformly in each successive instant of time from the breech to the muzzle, its intensity remaining the same. The question is, whether we can obtain mechanical power that will behave itself in such a manner as to do this work in this way.

3. *How Steam would do this Work.*—High pressure steam is exceedingly well adapted to the performance of this kind of work: unluckily it would require high pressure steam of 400 atmospheres or of 5000 lbs. pressure on the round inch, to perform this duty, and as such steam could only be generated in a furnace intensely heated, it is scarcely probable that boilers will be found sufficiently strong and durable to work continuously under such pressure. If they were found to be practicable, nothing more would be necessary than to bring a steam-pipe from the boiler to the breech of every gun in a fortress or a ship, and the admission of the charge of such steam into the chamber by a valve would be sufficient to discharge the missile of the 68-pounder with a speed of 1600 feet a second. The well-known Mr. Perkin studied this subject carefully, but applied it somewhat differently. He found that steam of this pressure could be generated only by heating the water nearly red-hot; and instead of throwing the steam into the breech by a pipe, he threw the red-hot water into the breech of his gun, allowing it when there to expand itself into steam, and expend its force in giving speed to the ball. This expedient of Perkins is well worthy of study. It has both the defects and the advantages of a gunpowder gun. The red-hot water thrown into the barrel would have the fault of being too powerful at the beginning of its expansion, and too weak at the end. The barrel

would be filled partly with water, and partly with steam; and as the water grew into steam it would lower its temperature and its pressure, so that the explosive force would fall off very much towards the end of the stroke. This is the inevitable evil of allowing the water to become vapour in the gun. When the steam is generated in a separate boiler, and freely admitted into the breech of the gun, there is reservoir enough of heat and steam to maintain the even pressure in following up the ball from the breech to the muzzle. It is the evil of charges converted into gas within the breech of the gun, that their temperature and pressure are too high at starting, and too low at the end. The steam-gun would in this respect be the best of our projectile forces.

4. *How Compressed Air would do the Work.*—Compressed air has many of the advantages and some of the defects of steam; and the frequent use of the air-gun has shown its convenience as well as its efficiency. Air can be compressed into a reservoir by mechanical force, just as steam can be raised in a boiler by heat; and by compressing 400 times the natural quantity of air into a given space a pressure of 400 atmospheres might possibly be obtained in this way. If an air pipe communicated from this reservoir to the breech of our gun, air of 400 atmospheres of pressure would certainly be able to follow up the 68-pounder shot, with pressure and velocity able to discharge it with a speed of 1600 feet per second, and, therefore, to do our work; but the apparatus would be full of mechanical difficulty.

5. *How Compressed Gases would do the Work.*—Liquid gases are known to be receptacles of enormous mechanical power. Carbonic acid gas, liquefied and shut up in a reservoir, generates large volumes of gas with great rapidity the moment it is permitted to expand. Other gases expand with still greater rapidity and force; and if we could conceive liquid gases to be easily made, safely carried, and comfortably handled, a charge of liquid gas, bottled up in the breech of a gun, would be a very effectual propelling power, and quite able to generate the force we want, and to apply it within the time we require. This system however is beset with mechanical difficulties.

6. *How Gunpowder and Gun-cotton would do the Work.*—The preceding illustrations of steam, compressed air, and liquid gases, lead us on very instructively to the manner in which fire has become necessary to do the work of a gun. A supply of heat is essential to the expansion of a gas, and a rapid supply is indis-

pensable to the rapid performance of the work. In steam, the fire was not only external to the gun, but external to the boiler in which the steam was generated. In gunpowder the fire is introduced into the inside of the gun, for the purpose of supplying the heat that is wanted to raise the gases to their elastic pressure, and to maintain them at that pressure while expanding. Red-hot steam introduced into the breech of a gun, rapidly cools down and loses its heat and power in expanding. If we could introduce fire into the breech of the gun at the same time, to maintain the heat of the steam and the water, the steam would become an admirable propelling force. Carbonic acid gas, expanding rapidly from the liquid into the gaseous state, cools down so suddenly as not only to lose its mechanical power, but to freeze into solid flakes of snow. If we could charge the breech of the gun with fire as well as with liquid gas, the fire would give it the heat it wants, prevent its congelation, and maintain its power to the end of the discharge. What gunpowder and gun-cotton do, is really to provide a reservoir of gas, and a fire to heat it simultaneously, and in the same chamber. In the case of gunpowder, the fire is fed with charcoal; in the case of gun-cotton, the fire is fed with the gun-cotton wool—another form of carbon. In gunpowder, large quantities of carbonic acid gas are generated, possibly in the liquid state, and are heated by the internal furnace of the charge, possibly red-hot. In like manner, in a gun-cotton charge, red-hot water or steam is introduced along with other gases, possibly also liquid, along with an internal furnace of flame; and thus the work is done—first, by the release of the gases themselves, and, secondly, by the continuance of the elasticity of those gases by the internal supply of heat. This is how gunpowder and gun-cotton really do the work of a steam gun, a carbonic-acid-gas gun, or any other kind of gas gun.

ON THE MEASURES OF THE POWER OF GUN-COTTON AND GUNPOWDER.

We have now seen that the work to be done in a 68-pounder naval cannon is the supply of a uniform force of 5000 lbs. per circular inch through a space of little more than 8 feet, during a time of $\frac{1}{100}$th part of a second. We have further seen that this can only be done by a pressure of gases to at least 400 atmospheres, and that these gases must not only be supplied at that pressure in sufficient quantities, but maintained at that pressure

by the equally rapid development of a large supply of heat. When, therefore, we compare the value of gunpowder of one sort with gunpowder of another sort, or with gun-cotton, the radical question will really be which contains the best supply of gases, and which maintains them best at the required temperature and pressure; and in considering these questions, we must also consider that we may have too much pressure as well as too little, and that what is best for us in artillery is really to have the force we want, applied with perfect uniformity, so as to have neither more nor less than the pressure required to produce the speed we seek. The reason of this is the durability of the gun. The life of a gun depends upon its never being more strained than the least that is necessary, by a uniform action along the barrel, to acquire the terminal speed. Any variation in the moving pressure must either impair the speed or impair the gun.

1. *Whether Gunpowder or Gun-cotton is the best producer of Gases.*—The answer to this question is, that 1 lb. of gun-cotton produces as much gas as 3 lbs. of gunpowder. The reason of this is, that in gunpowder a large portion of the materials put into the breech of the gun to supply fire and to supply gas, leave behind them a large quantity of refuse or rubbish, so that only one-third of the whole is good, useful, propelling gas and heat. It is the refuse, therefore, of gunpowder which constitutes its disadvantage. This refuse remains partly in the barrel of the gun, which it fouls, and partly is thrown out of the gun behind the ball, where it is diffused among the air, in smoke and soot, which obstruct the view and choke the breath of the men, and waste the power which has to throw it out of the gun. Gun-cotton, on the contrary, produces flame and gas, and nothing else. When you set fire to the cotton, it generates flame, developes gas, and the whole products of combustion consist in either pure gases, or liquids which are converted into gases, and constitute the moving power which propels the shot: there is no rubbish and no residue: there is no fouling in the gun, and no smoke from its muzzle. A little water settling in dew-drops on the inside of the gun, and a little steam issuing from its muzzle, is all the residue to be detected after the discharge of a gun-cotton cannon.

In order to understand how this comes about, we have only to recur for a moment to the analyses of the component parts and of the explosive products of gunpowder and gun-cotton, as they are given in the chemical part of this work. Taking 100 lbs. of

gunpowder and 100 lbs. of gun-cotton, we find the following as their composition :—

Components.

Gunpowder.		Gun-cotton.
12·5	Sulphur	None.
30·0	Potash	None.
12·5	Carbon	25·30
None	Hydrogen	3·12
10·0	Nitrogen	12·60
35·0	Oxygen	60·00
100 lbs.		100 lbs.

After explosion has taken place under pressure, we find the following products :—

Products.

Gunpowder.		Gun-cotton.
56	Sulphate of potash and Carbonate of potash	None.
12	Various salts	None.
Solids 68		Solids none.
10	Nitrogen	13
20	Carbonic acid gas	28
None	Carbonic oxide gas	29
2	Sundry gases	5
None	Water or Steam	25
32		100

It appears, therefore, that out of 100 lbs. of gunpowder, 68 lbs. are solid refuse, and 32 lbs. are gases, while 75 lbs. are gases in the case of gun-cotton, and the remaining 25 lbs. are water, turned, of course, into high-pressure steam at the high temperature of the combustion chamber. There can be no doubt, therefore, that gun-cotton, as a producer of gases, is more fertile than gunpowder in the ratio of 3 to 1.

2. *On the relative Strength of Gunpowder and Gun-cotton.*— Having now determined that 100 per cent. or the whole contents of gun-cotton are elastic gases, capable of exerting high propelling power, and that only 32 or 33 per cent. of the whole weight of

gunpowder consists of such gases, we have next to ask—Which of these supplies the gases in the manner best fitted for our practical use? The practical usefulness of a gas for propelling power depends mainly on the room it occupies, and on the room which it is able to occupy. It is to this measure that we are in the habit of applying the term "atmospheres of pressure." This term we apply to all gases indiscriminately. We apply it under a law which is called Marriotte's. The law of Marriotte is this:—that if we take a cubic foot of gas—common air, for example, of the atmosphere—and compress that air into half its bulk, it will in this half-bulk produce a pressure of two atmospheres; if we press it into one-fourth of its bulk, it will produce a pressure of four atmospheres; compressed into one-tenth of its bulk, it will expand with a force of ten atmospheres; and to a hundredth part of its bulk, it will resist with a force of one hundred atmospheres. Common air has an ordinary pressure, not exceeding 15 lbs. on the square inch: this we call the pressure of the atmosphere. If we took a cubic foot of air, and could squeeze it into the bulk of $\frac{1}{400}$th part of a cubic foot, it would exert a pressure of 400 times 15 lbs., or equal to 6000 lbs. on the square inch, or 5000 lbs. on the round inch, which is just the force we are seeking. What we want, therefore, from gunpowder and gun-cotton is, that they should furnish us with a continuous and even supply of gases compressed to 400 atmospheres or 6000 lbs. per square inch: the question therefore is, whether gunpowder and gun-cotton can possibly yield us these supplies. It would help us to arrive at this conclusion, for gun-cotton at least, to remember that gun-cotton contains 25 lbs. of water to 100 lbs. of cotton, in addition to 75 lbs. of other gases. Now water consists of steam compressed into $\frac{1}{1728}$th part of its bulk: in other words, water is steam compressed 1728 times. Of course, if steam could be compressed into this bulk, and still remain steam, we might obtain this force out of it; but we have reason to believe that steam has actually been generated in the state we call red-hot steam, so as to be exactly double its bulk of water, still retaining the state of steam: we may, therefore, expect to have steam of 864 atmospheres of pressure, provided we can heat it red-hot, or a pressure of 12,960 lbs. per square inch. Here, then, we have a large supply of an elastic gas of adequate power, without taking into account the remaining 75 per cent. Turning now to the gases of gunpowder, we find that they amount to 32 per cent. of gases similar to the remain-

ing gases of gun-cotton—similar, but not identical. We find that 32 lbs. of gases of gunpowder are capable of producing 320 cubic feet of gas, while the remaining gases of gun-cotton produce 1000 cubic feet; and we also find that the 320 cubic feet of gases occupy 1·2 cubic feet, while the 1000 cubic feet of gun-cotton gas occupy 4 cubic feet; 100 lbs., therefore, of gunpowder gases give us 320 cubic feet, bottled up in 1·2 feet, while 1000 cubic feet of gun-cotton gases are bottled up in 3$\frac{1}{3}$ths cubic feet. From this we readily draw the following conclusion:—that in the bulk of gunpowder these gases, if simply set free, would exercise a pressure of 266 atmospheres, while in gun-cotton they would exercise a pressure of 275 atmospheres. From this comparison, made on the basis of Marriotte's law alone, and treating the gases without reference to temperature in either case, we draw the following conclusions:—First, that the gases of gunpowder and the gases of gun-cotton are nearly equally good as projectile forces, and nearly equally strong. Secondly, we learn that it is the water contained in the gun-cotton which alone can confer upon it greater propelling power, and greater elastic pressure than gunpowder; and that without this element of steam in gun-cotton, there would be no mechanical reason why the gases of gun-cotton should yield a better result than the equal weight of gases of gunpowder. Taken apart from its steam power, the gases of gun-cotton would give to it three times the power of gunpowder, merely because two-thirds of gunpowder in weight are solids, and not gases, and therefore of little use in propulsion; and not merely of little use, but as, immediately after the shot, they are thrown out of the gun with a velocity due to the whole remaining elastic force of gunpowder, there is mechanical power lost in the very act of propelling the gunpowder refuse. We now come to this practical conclusion, that if in the same bulk of charge as gunpowder we put one-third of the weight of gun-cotton, its permanent gases alone should give it the same propelling power as gunpowder. Let us not forget, however, that by adding to the 75 lbs. of gun-cotton gases, the 25 lbs. of water, we have 25 lbs. capable of exerting a pressure of 864 atmospheres—nearly three times the pressure of the other gases. Let us remember also, that in doing this we only add $\frac{1}{3}$ths of a cubic foot to the space occupied by the gun-cotton, and that we add 690 cubic feet to the volume of the gases: we have altogether, therefore, 1690 feet of gas and steam in a volume of 4 cubic feet, which together would give us a mean pressure of

422 atmospheres, instead of, as in gunpowder, 266, or as in the gun-cotton gases, without the steam, 275 atmospheres. In conclusion, we have already shown that what we want in order to give a 68 lb. shot, a speed of 1600 feet a second, is a pressure of 400 atmospheres; and we have now got from gun-cotton a pressure of 422 atmospheres, calculated by Marriotte's law alone. We have carefully, up to this point, avoided the introduction of calculations involving temperature. The phenomena of temperature which take place in the breech of a gun during the instant of explosion are utterly unknown, and possibly incomprehensible; but what we have shown is, that without the aid of any higher temperature than is necessary to maintain these gases at a temperature due to their elasticity, gun-cotton is able to supply the force we want: that gunpowder is unable to supply that force by mechanical pressure merely; and that it can, therefore, only be produced by raising the charge in the chamber of the gun to an extremely high temperature. This reveals to us another peculiarity of gun-cotton—that it does not communicate that intense temperature to the gun which gunpowder is well known to communicate, and that, therefore, the gun can be worked rapidly, continuously, safely, and cleanly with gun-cotton, when rapid firing becomes impossible owing to the heat and dirt of gunpowder. So far, therefore, we trust we have some insight into the nature and mechanical power of gun-cotton, and the causes of its difference from gunpowder.

In conclusion, it is only necessary to remark that 100 lbs. of gunpowder occupy 1·8 feet, or 55·5 lbs. occupy 1 foot: also, that 100 lbs. of gun-cotton occupy 4 feet, and 25 lbs. occupy 1 foot. Next, that the 68 lbs. of solids of gunpowder fill $\frac{7}{10}$ths of a foot, while the gases of gunpowder occupy $1\frac{3}{10}$ths of a foot: the 25 lbs. of water in gun-cotton occupy $\frac{4}{10}$ths of a foot:—or

		Cubic feet.
100	lbs. gunpowder	= 1·8
100	lbs. gun-cotton	= 4·0
55·5	lbs. gunpowder	= 1·0
25	lbs. gun-cotton	= 1·0
68	lbs. solids-gunpowder	= 0·6
32	lbs. gases-gunpowder	= 1·2
25	lbs. water-gun-cotton	= 0·4

ON THE MANNER OF USING GUN-COTTON AND GUNPOWDER FOR PURPOSES OF ARTILLERY.

The following are the objects we must steadily have in view in order to serve artillery with an explosive force in the manner best adapted for our use.

1. *How not to burst the Gun.*—If bursting the gun were one of the objects intended by charging it with gunpowder, the best way to do it would be to fill it with the finest and strongest powder compressed into the least bulk, and to oppose some resistance to the projectile leaving the gun, so that the shot should not travel far until the whole of the gaseous portion of the gunpowder was fully developed; and if after this we let go the shot, so that it could travel freely along the barrel, with the whole of the elastic gases fully developed, but confined behind it, that would be the best way of getting the whole virtue out of the gunpowder and out of the gas; but it would assuredly be the best way also to burst the gun. If, therefore, gunpowder were dearer than guns, and we wanted to economize powder at the cost of guns, this would be the best way to set about it. The way, on the contrary, not to burst the gun, is so to insert the shot, that it shall move easily and without impediment away from the breech, at the very earliest instant when the charge has begun to burn; that the charge shall burn so fast, and no faster, than to keep the gun behind the ball filled with gas of the required density; the consequence of which will be that at no time will there be more force exerted on the gun than is absolutely necessary to propel the shot, and this we have seen is 5000 lbs. per circular inch, or 6000 lbs. per square inch, or 400 atmospheres.

Two modes present themselves of adopting explosive charges to effective propulsion without injury to the gun. The two modes are—never to allow the initial pressure on the shot to be excessive at starting, and never to permit the propelling power to fall away before the shot leaves the gun; in short, the object is, to maintain steadily and uniformly the least pressure that will do the work. In gun-cotton, the way to avoid too great initial pressure, is to take care that the gun-cotton have sufficient room in the chamber; it should have even more than double the room which it naturally occupies; for if you put the whole 25 lbs. of the gun-cotton into 1 cubic foot of space, you get twice as much force as you want. For this purpose, there should never be more than

11 lbs. of gun-cotton to a cubic foot of gun-chamber; and even less would produce the same effect as gunpowder. By putting double the quantity of gun-cotton into the same space, you would double at least the initial force of explosion, and burst the gun. In addition to giving it room, arrangements may with advantage be made in the cartridge, to prevent it from lighting more rapidly than is necessary to maintain the uniform pressure. The enclosure of the cartridge in distinct concentric layers or tubes, gives us a method of entirely commanding the rate of combustion of the gun-cotton charge.

With Gunpowder a different method is necessary. Too much room for the charge is often said to be a means of bursting the gun. Instead of giving the powder room, what is necessary, is, to condense it as much as possible, so that the flame shall not rapidly get at the heart of the powder; that it shall, therefore, be burnt slowly, and so give a more continuous and moderate propelling power. This is called slow-burning or cake powder, and it also saves the gun.

2. *How to form a Gun-cotton Cartridge.*—A gunpowder cartridge is little more than a measure of powder, to limit the quantity of the charge that is necessary for use; the cartridge in no way modifies the effect of the charge. A gun-cotton cartridge, on the other hand, is a curiously-contrived piece of mechanism intended to propel the shot and spare the gun. For a small rifle gun, the charge is a hollow cotton tube, woven like a common wick, and kept open in the middle by a *papier maché* tube of strength enough to support the cartridge and prevent the cotton from being crammed into less bulk; in short, to give it room; a wooden tube is even more effectual for this purpose; and so a gun-cotton cartridge is liker to a lady's bobbin of sewing silk than to a gunpowder cartridge. On the large scale of a cannon, the cartridge consists of a hollow wooden pipe for a core; round this pipe the cotton yarn is carefully coiled by special machinery, and layer after layer wound on, until its diameter fills the space of the chamber of the gun, when it is enclosed in a flannel bag like the ordinary gun cartridge. It is this mechanical structure which enables us to regulate the performance of a gun-cotton cartridge. We may wind on the gun-cotton on its core either lightly or under pressure; we may enclose layer after layer more strongly or less completely; we may give the cartridge a dense core and an open skin, or enclose an open core in a dense tube; by very simple

mechanical manipulation, we can thus make the rate of combustion and the volume of gas produced just what we please. This is one of the great virtues of gun-cotton.

3. *On the Manner of using Gun-cotton for Destructive Purposes.*—By destructive purposes we mean, that the end in view shall be to destroy the chamber which contains the cotton charge instead of using it as a cylinder for producing motion; in short, to exploding mines, working quarries, destroying structures, and removing obstacles. Here we are met at once by a remarkable contrast between gun-cotton and gunpowder. To burst a gate by gunpowder, you merely nail a flannel bag containing 50 lbs. of gunpowder, on the gate, light it by a match, retire, and the gate is burst open. A bag of gun-cotton similarly fired would be perfectly harmless. To destroy a wooden bridge, it would only be necessary to pile on its upper surface a few such bags of gunpowder, and by firing them it would be destroyed; a palisade is often thrown down in like manner. Treated in this way, gun-cotton is perfectly ineffectual.

4. *How to destroy the Chamber.*—Now, to use gun-cotton to the same destructive effect, it is merely necessary to treat it in another way. Take 25 lbs. of gun-cotton rope, and, instead of giving it room as you did in the gun, put into an opening, or a barrel, or the chamber of a gun, or the bore-hole in a quarry, the greatest quantity it will hold in the densest form, and its force will be found inconceivably greater than either an equal quantity or an equal weight of gunpowder. To blow down the gate, you need only put 25 lbs. of gun-cotton into a cylindrical box of iron, and it will blow up the gate with greater effect than six times the weight of gunpowder. Throw down an iron cylinder, containing 25 lbs. of gun-cotton, in front of a row of palisades, from one to two feet diameter; it will shatter them within a range of six feet into matches. Fill the breech of any gun with dense gun-cotton, and it will burst the gun, even without a bolt. Place a 25-lb. box of gun-cotton on a timber railway bridge, it will shiver it to pieces. Explode 500 lbs. of gun-cotton in an iron cylinder under the bottom of a ship of war, and it will cease to be a ship; but in every case you must see that the gun cotton ropes are dense, that they are perfectly enclosed in the chamber, that the chamber is strong enough to resist explosive pressure until the whole charge is in full combustion, and the effect will be greater than gunpowder, in the proportion at least of 6 to 1.

General Lenk's Discoveries.

The mechanical application of gun-cotton may be considered to be due exclusively to Major-General Lenk, of the Austrian service. Pure gun-cotton becomes either a powerful explosive agent, or a docile performer of mechanical duty, not according to any change in its composition, or variation in its elements or their proportions, but according to the mechanical structure which is given to it, or the mechanical arrangements of which it is made a part. It was General Lenk who discovered that structure was quality, and mechanical arrangement the measure of power, in gun-cotton; and in his hands, a given quantity of the same cotton becomes a mild, harmless, ineffectual firework, a terrible, irresistible, explosive agent, or a pliable, powerful, obedient workman.

The *first* form which General Lenk bestowed on gun-cotton, was that of a continuous yarn or spun thread. Gunpowder is carefully made into grains of a specific size. Gun-cotton is simply a long thread of cotton fibre, systematically spun into a yarn of given weight per yard, of given tension, of given specific weight. A hank of a given length is reeled, just like a hank of cotton yarn to be made into cloth, and in this state gun-cotton yarn is bought and sold like any other article of commerce.

This cotton yarn converted into gun-cotton, may be called, therefore, the raw material of commerce. In this form it is not at all explosive in the common sense of the word. You may set fire to a hank of it, and it will burn rapidly with a large flame; but if you yourself keep out of the reach of the flame, and keep other combustibles beyond reach, no harm will happen, and no explosion or concussion will result. If you lay a long thread of it round your garden walk at night, disposing it in a waving line with large balls of gun-cotton thread at intervals, and light one end of the thread, it will form a beautiful firework, the slow lambent flame creeping along with a will-o'-the-wisp-looking light, only with a measured speed of 6 inches per second, or 30 feet a minute; the wind hastening it or retarding it as it blows with or against the line of the thread. This is the best way to commence an acquaintance with this interesting agent.

Care must be taken not to become too familiar with gun-cotton even in this harmless and playful guise; cotton dresses will readily catch fire from it, and it should not be treated with less care to

keep fire from it than gunpowder. In one respect it is less liable to cause danger than gunpowder. Grains of powder are easily dropped through a crevice, and may be sprinkled about in a scarcely noticeable form, but a hank of gun-cotton is a unit, which hangs together and cannot strew itself about by accident.

The *second* form of gun-cotton is an arrangement compounded out of the elementary yarn. It resembles the plaited cover of a riding-whip; it is plaited round a core or centre which is hollow. In this form it is match-line, and, although formed merely of the yarn plaited into a round hollow cord, this mechanical arrangement has at once conferred on it the quality of speed. Instead of travelling, as before, only 6 inches a second, it now travels 6 ft. a second.

The *third* step in mechanical arrangement, is to enclose this cord in a close outer skin or coating, made generally of India-rubber cloth, and in this shape it forms a kind of match-line that will carry fire at a speed of from 20 to 30 feet per second.

It is not easy to gather from these changes what is the cause which so completely changes the nature of the raw cotton by mechanical arrangement alone. Why a straight cotton thread should burn with a slow creeping motion when laid out straight, and with a rapid one when wound round in a cord, and again much faster when closed in from the air, is far from obvious at first sight; but the facts being so, deserve mature consideration.

It is a *fourth* discovery of General Lenk, that to enable gun-cotton to perform its work in artillery practice, the one thing to be done is to "give it room." Don't press it together—don't cram it into small bulk! Give it at least as much room as gunpowder in the gun, even though there be only one-third or one-fourth of the quantity, measured by weight. 1 lb. of gun-cotton will carry a shot as far as 3 or 4 lbs. of gunpowder; but that pound should have at least a space of 160 cubic inches in which to work.

This law rules the practical application of gun-cotton to artillery. A cartridge must not be compact, it must be spread out or expanded to the full room it requires. For this purpose, a hollow space is preserved in the centre of the cartridge by some means or other. The best means is to use a hollow thin wooden tube to form a core; this tube should be so long as to leave a sufficient space behind the shot for the gun-cotton. On this long core the simple cotton yarn is wound round like thread on a bob-

bin, and sufficiently thick to fill the chamber of the gun; indeed, a lady's bobbin of cotton thread is the innocent type of the most destructive power of modern times—only the wood in the bobbin must be small in quantity in proportion to the gun-cotton in the charge. There is no other precaution requisite, except to enclose the whole in the usual flannel bag.

The artillerist who uses gun-cotton has therefore a tolerably simple task to perform if he merely wants gun-cotton to do the duty of gunpowder. He has only to occupy the same space as the gunpowder with one-fourth of the weight of gun-cotton made up in the bobbin as described, and he will fire the same shot at the same speed. This is speaking in a general way, for it may require in some guns as much as ⅓rd of the weight of gunpowder and ⅓ths the bulk of charge to do the same work; a little experience will settle the exact point, and greater experience may enable the gun-cotton to exceed the performance of the gunpowder in every way.

The *fifth principle* in the use of gun-cotton is that involved in its application to bursting uses. The miner wants the stratum of coal torn from its bed, or the fragment of ore riven from its lair: the civil engineer wishes to remove a mountain of stone out of the way of a locomotive engine; and the military engineer to drive his way into the fortress of an enemy, or to destroy the obstacles purposely laid in his way. This is a new phase of duty for gun-cotton—it is the work of direct destruction. In artillery you do not want to destroy directly, but indirectly. You don't want to burst your gun, nor even to injure it; and, we have seen, in order to secure this, you have only to give it room.

The fifth principle, therefore, is, to make it destructive—to cause it to shatter everything to pieces which it touches, and for this purpose you have only to deprive it of room. Give it room, and it is obedient; imprison it, and it rebels. Shut up without room, there is nothing tough enough or strong enough to stand against it.

To carry this into effect, the densest kind of gun-cotton must be used. It must no longer consist of fine threads or hollow textures wound on roomy cores. All you have to do is to make it dense, solid, hard. Twist it, squeeze it, ram it, compress it; and insert this hard, dense cotton rope, or cylinder, or cake in a hole in a rock, or the drift of a tunnel, or the bore of a mine; close it up, and it will shatter it to pieces. In a recent experi-

ment, 6 ounces of this material, set to work in a tunnel, not only brought down masses which powder had failed to work, but shook the ground under the feet of the engineers in a way never done by the heaviest charges of powder.

To make gun-cotton formidable and destructive, squeeze it and close it up; to make it gentle, slow, and manageable, ease it and give it room. To make gunpowder slow and gentle, you do just the contrary: you cake, condense, and harden it to make it slow, safe for guns, and effective.

To carry out his principle successfully, you have to carry it even to the extreme. Ask gun-cotton to separate a rock already half separated, it will refuse to comply with your request. Give it a light burden of earth and open rock to lift, it will fail. If you want it to do the work, you must invent a ruse,—you must make believe that the work is hard, and it will be done. Invent a difficulty and put it between the cotton and its too easy work, and it will do it. The device is amazingly successful. If the cotton have work to do that is light and easy, you provide it with a strong box, which is hard to burst, a box of iron for example; enclose a small charge, that would be harmless, in a little iron box, and then place that box in the hole where formerly the charge exploded harmless, and in the effort it makes to burst that box, the whole of the light work will disappear before it.

General Lenk's Experiments.

In a long series of experiments made by General Lenk in Austria, answers were obtained to the following questions:—

1. *On recoil.*—Chiefly on account of the smaller space of time the projectile requires to pass through the barrel of a gun, to attain a certain initial velocity, the recoil of the gun is less than with the use of gunpowder. It may be stated that, by the official trials of the Commissioners in the year 1860, the recoil of the gun with gun-cotton was found to be 0·68 of that with gunpowder.

2. *Whether Gunpowder or Gun-cotton admits of most rapid firing?*—The gun, being heated considerably less by using cotton cartridges, the absence of a noteworthy residuum and smoke, admits of a more easy manipulation and sighting of the gun, and thereby secures a more continuous and rapid fire.

It may be stated that 100 rounds with gun-cotton were fired in 34 minutes, and the barrel was heated to 50° C.; whilst 100 rounds with gunpowder cartridge in 100 minutes, heated the gun

so much that water, dropped on the barrel, immediately evaporated with noise, though three times as much time was required with the powder charges. The Commissioners continued the trials with gun-cotton up to 180 rounds without any danger from heating being apprehended, whilst they thought it advisable, for the sake of safety, not to continue firing with powder charges under the above circumstances.

3. *What advantages it has in continuous firing and breech-loading?*—It has been already mentioned that, with the use of gun-cotton, fire-arms remain considerably cooler than with gunpowder; and the slight residuum has no influence upon the effect of the gun.

There being no fouling of the gun, it follows that, with the use of breech-loaders, the construction of the breech may be kept quite tight.

Under all circumstances, the aim is not disturbed or interrupted, there being no smoke attending the discharge of the gun.

4. *On its advantages for forts, ships, and casemates.*—From many experiments, but especially from the official trials made in the casemates of the fortress of Comorn in the year 1853, it results that, under circumstances which would render the firing with powder difficult or even impossible, there was no trouble or molestation in any way to those serving the guns with the use of gun-cotton cartridges.

The trials in the fortress of Comorn were made in casemates, ventilation being intentionally obviated. After fifteen rounds with powder cartridges, further sighting of the gun was impossible; after forty-six rounds, one of the men serving the gun fell into convulsions of suffocation; a second man being ordered in the place of the first disabled man, became immediately sick on entering the casemate; the rest of the men were more or less stupified; it was necessary to stop firing after fifty rounds, given in eighty minutes. By using gun-cotton cartridges, on the contrary, after fifty rounds, the men serving the gun felt not the least molestation, and the aim was always clearly visible.

5. *On its use in channels.*—Shells filled with gun-cotton hold a considerably larger quantity of material for the production of gases; at the same time, it is in the nature of both compounds that gun-cotton developes far more quickly the gases of combustion than gunpowder; for this reason, shells filled with gun-cotton burst into at least double the number of pieces.

6. *On its Use in Smooth-bore Guns.*—The standard of reference was furnished by experiments conducted with a 12-pounder bronze field piece, which gave results as follows :—

The weight of shot, solid round, used was 12 lbs.

Diameter of shot 4·5 inches. (English weight and measure.)

Diameter of bore for gun-cotton 4·56 inches.

Diameter of bore for gunpowder 4·67 inches.

Result.	Gun. No	Gun. Length of Bore.	Cartridges. Material of Charge.	Cartridges. Length.	Initial Velocity.	General Observations.
I.	..	13½ calibres.	Powder 3 lbs. 1 oz.	7·5 in.	1400 ft.	Normal.
II.	2	11½ ,,	Gun-cotton. 13·6 oz.	5·1	1375	Cartridges slightly compressed, filling the whole space.
III.	,,	11½ ,,	,, 14·8	,,	1407	
IV.	3	10½ ,,	,, 13·6	,,	1358	
V.	1	11½ ,,	,, 14·8	8·3	1400	Hollow cartridges.
VI.	1	10 ,,	,, 15·9	,,	1426	
VII.	1	9 ,,	,, 17·0	,,	1402	

The normal performance of ordinary powder-guns gives Result I., as compared with gun-cotton. With gun-cotton, when compressed charges were used, each of 13·6 oz., Result II., Gun 2 ; the gun was not injured ; while with 14·8 oz. of charge, after a few rounds, a considerable enlargement of the bore, where the shot lies, took place. A similar result happened to a second gun, No. 3, even with a charge of 13·6 oz., after the first shots.

When one of the enlarged cartridges was used, occupying 1·1 of the powder-space, the gun's endurance was perfect, and no loss of effect was sustained, and its practice remained good, as proved by results set forth at III. and V., since *equal charges* in *very different spaces* (*i. e.* in the ratio of 5 to 8) still produced equal results.

In proportion as the tube is shorter, an increased charge is required (shown by Results V., VI., VII.) ; yet the effect of a normal powder-gun and charge may be attained by a tube shortened from 13½ to 9 calibres : it follows that guns to be used with gun-cotton may be constructed much shorter than if intended to be charged with gunpowder.*

With the largest charge used, *i. e.* 17 ounces, about 1000 shots were fired from the same gun, without affecting the piece in the slightest—an endurance very satisfactory, and considerably greater than has been experienced with gunpowder.

This experiment was further continued for arriving at results

* No details are given as to precision.

by empirical means as to the strength of metal in various parts of the tube.

The original tube was gradually turned off, but without any disadvantageous effect. The metallic strength of 3·7 inches close behind the seat of the ball, where, according to experience, the greatest strain takes place, and 1·6 inch at the muzzle, was so moderate that for practical uses no further diminution was desirable; hence the experiments in this respect were discontinued.

Finally, I turned my attention to the object of flattening the trajectory of projectiles, and succeeded with spherical excentric shot to such an extent, that a projectile fired from the gun horizontally, pointed at targets set up at 100 yards from each other as far as 1200 yards, struck at an *even height* at 3 feet from the ground, and fell *without ricochet* at about 3200 yards.

An experiment made with a Krupp cast-steel 6-pounder, demonstrated that with harder and more resisting metal than bronze, the great power of gun-cotton might unhesitatingly be made use of to obtain a more energetic projectile force than would have been compatible with the use of gunpowder.

The results are as follows:—

A Krupp 6-pounder, cast-steel, charged with 30 oz. of normal powder . .	1338 ft. per second initial velocity of shot.
A Krupp 6-pounder, cast-steel, charged with 13½ oz. of gun-cotton . . .	1563 ft. per second initial velocity of shot.

In practice it is necessary, with the use of gun-cotton, to reduce the "windage" to a minimum; otherwise larger charges must be used, and with no corresponding advantage.

7. *On its Use in Rifle Guns.*—The time may have arrived for breech-loaders, which have lately come into use under such good auspices, to be set aside in favour of muzzle-loaders, for the service of which gun-cotton offers such facilities, because of its leaving no solid residue after combustion, and because windage admits of reduction to a minimum.

The method of determining the condition of charge, differs from the data given for smooth-bores, in so far that the vehemence of explosion may be decreased by mechanical means—such as variation of length of chamber, regulating the mode of ignition so as to attain a sufficiently favourable condition of starting of the projectile from rest. This result was easily achieved (as demonstrated

by experiments conducted in Austria) within the degrees of velocity hitherto deemed sufficient.

To what extent these deductions may hold good at higher velocities, must be determined by further experiments, which may be expected, judging from present data, to give favourable results.

The Austrian breech-loading guns (cast-iron) of three service calibres (6, 12, and 24-pounders, charged with 13, 30, and 60 lbs. weight projectiles respectively,) answer perfectly when charged with gun-cotton, provided the chambers are enlarged to 1·1 of the original capacity for powder. For larger charges, cartridges made in the form of a hollow rope, similar to those used for blasting, would answer; however, I have to remark that it is more necessary in rifled than in smooth-bore guns to reduce the windage to a minimum; this, on account of the surprising exactness of work in English factories, would be easy of accomplishment, and would raise the effect of gun-cotton. Experiments performed with a cast-steel gun of 3 inches diameter, weighing only 50 lbs., firing hollow projectiles with effect to 3000 yards, demonstrate that, on account of the short length of tube necessary and the slight recoil, very light pieces can be made; the carriage was about 40 lbs. weight.

8. *On its Application to Small Arms.*—In this respect it is important to observe that the plasters used with the old round-ball rifles were completely torn so long as short cartridges were used. When the cartridges were elongated, the plasters resisted perfectly, and practice was very accurate; hence it is demonstrated that *length* is a very important element in the construction of small-arm cartridges. Experiment only can determine the *proper* length.

One circumstance is not to be lost sight of—that with a *very* long cartridge, the *ignition* of it in proper time may be difficult to achieve. Practice in the application of mechanical means is requisite to secure the proper explosion of long cartridges by igniting them *well* in front. Lastly, experience proves that in small-arm cartridges, *separation* of the cotton into several layers, by the interposition of paper, influences the result. Small-arm cartridges which have answered best, are composed of three layers of flat woven gun-cotton with paper interposed. For the small-bore long-range rifles used in England, the cartridges most suitable must have their precise dimensions fixed experimentally.

On the 4th and 5th of July, 1863, there was a preliminary trial at Manchester, during which it was found that no distortion of the projectiles ensued even when the proper conditions of charge were departed from by using too heavy charges.

9. *On its Application to Mines.*—Gun-cotton is more appropriate to this use than gunpowder, which it surpasses in proportion as the mass to be blasted is more compact. Assuming a solid rock to be blasted, and that due attention has been paid to the proper condition of charge together with the proper distribution of holes, the relative proportions of gun-cotton and of gunpowder for producing an equal effect are 1 of gun-cotton to 6·274 of gunpowder (weight by weight), whilst the relative proportions for wall-blasting (masonry) are 1 of gun-cotton to 2·25 of gunpowder; however, here the point must be noted, that when these experiments were performed, the *best shape* of charge had not been determined. According to experiments more recently conducted, the form of charge for blasting which answers best, is that of a *hollow twisted rope*, according to sample; the operation of charging is thus rendered very easy and safe—wooden tamping-rods being used until the charge is covered. According to repeated experiments, the strongest friction of gun-cotton between stone is unattended with the slightest danger. For large charges, it is to be remembered that *complete* ignition is more difficult than the complete ignition of large powder charges; to accomplish this result satisfactorily for mining purposes, it is indispensable to fasten up the gun-cotton in *tightly closed vessels*—which afford the necessary resistance, *not yielding until the whole mass of gun-cotton has become ignited.* Experiments have proved that little barrels with strong hoops answer best. The proper construction of these restraining cases can be learnt experimentally from models, when it will be remarked that *no smoke* results from explosion, and *very little fire* is seen.

EXPERIMENTS ON BLOWING UP BRIDGES.

First Trial.

Four 6 × 8 inch beams of fresh wood placed across two sills, bound by ten iron rivets to the sills, fastened with pegs, and laid over a ditch 1 fathom long. In the centre of this combination of beams is an explosive box charged with 25 lbs. of gun-cotton of 0·371 density, fired by electricity (Figs. 217, 218, 219). Fig. 220 shows its condition after the explosion. Several beams were com-

FIG. 217.

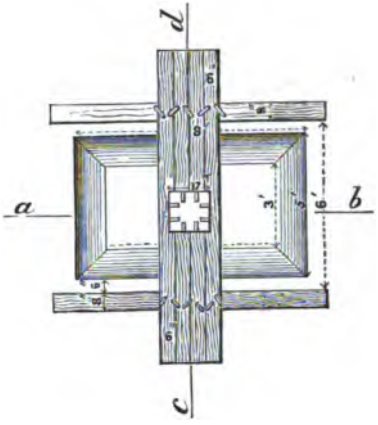


FIG. 218.

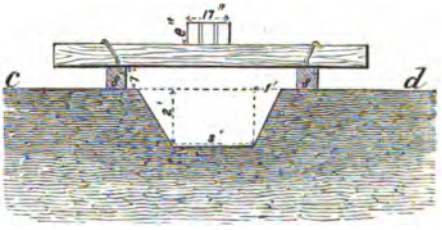
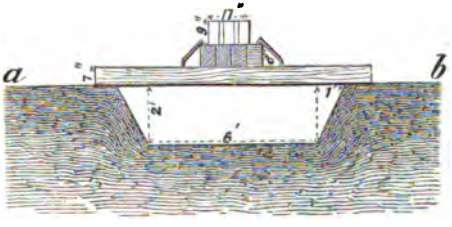


FIG. 219.



pletely shattered from end to end and thrown partly into, partly round the ditch; even the iron rivets were broken in pieces.

Second Trial.

A bridge was constructed 4 fathoms long and 10 feet wide, of four 10 × 12 inch beams, as in Fig. 221, over which a 1½ inch cover of planks was fastened by means of six 7-inch binding-sills

FIG. 220.

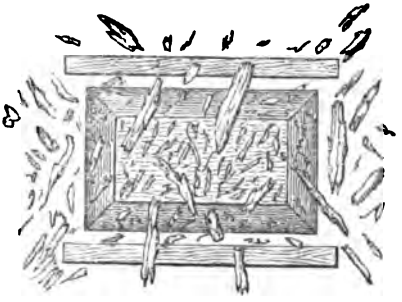
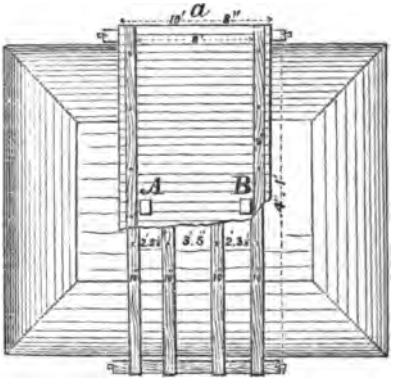
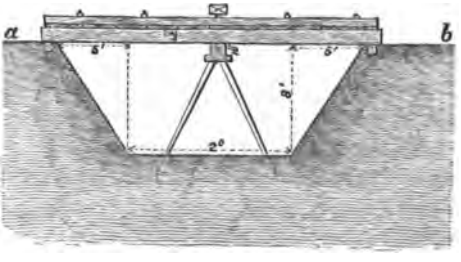


FIG. 221.



and iron screws (Fig. 221). The centre of the bridge was strengthened by a trestle of 4 inches of trunkwood. Two explosive boxes, A, B, each with a 25 lb. charge of gun-cotton 0·371 density, constructed as before, were placed over the trestle on the edge of the bridge (Fig. 222) and fired simultaneously by means

FIG. 222.



of a quick-match. Only the box A took effect, as shown in Fig. 223. It broke the trestle, the binding-sill, and the underly-

FIG. 223.

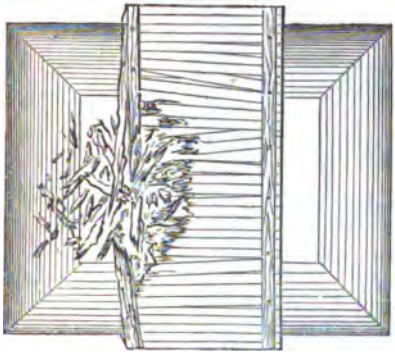
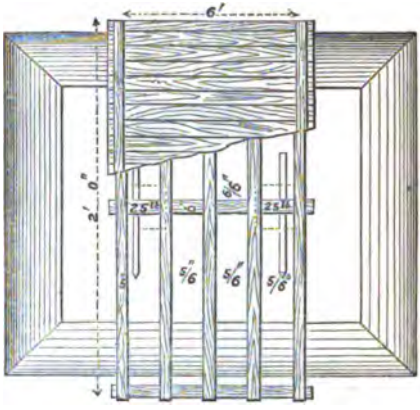


FIG. 224.

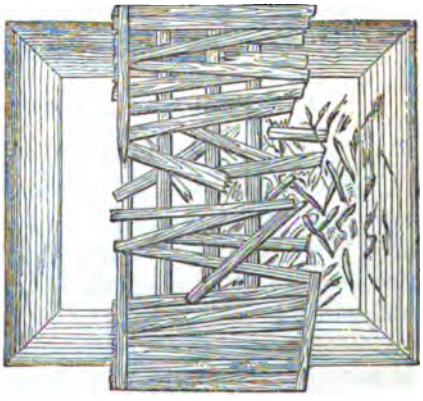


ing beam, and destroyed part of the covering. B was hurled away, and exploded in the air.

Third Trial.

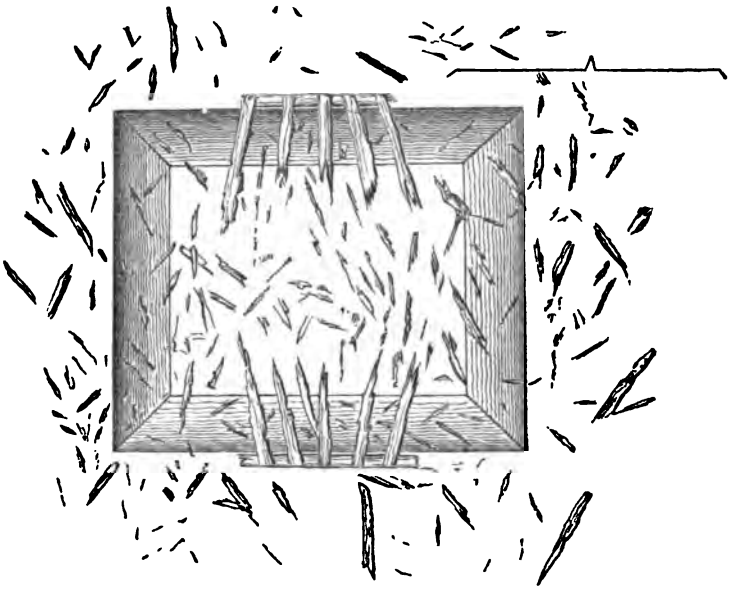
Two bridges were constructed, as in the former experiment, being two fathoms long and one broad, and blown up in the manner first described, by two explosive boxes of gun-cotton, with a charge of 25 lbs., and lighted, in the first experiment by a quick-match, in the second by electricity. Each bridge was constructed as in Fig. 224 of five 5 × 6 inch beams, fastened over with a 1½ inch covering of posts, and strengthened in the centre by a strong trestle. Only one of the explosive boxes took effect when lighted by the quick match (Fig. 225). It broke the trestle, one beam,

FIG. 225.



and destroyed part of the covering. But both explosive boxes took effect when fired by electricity (Fig. 226), where they were

FIG. 226.



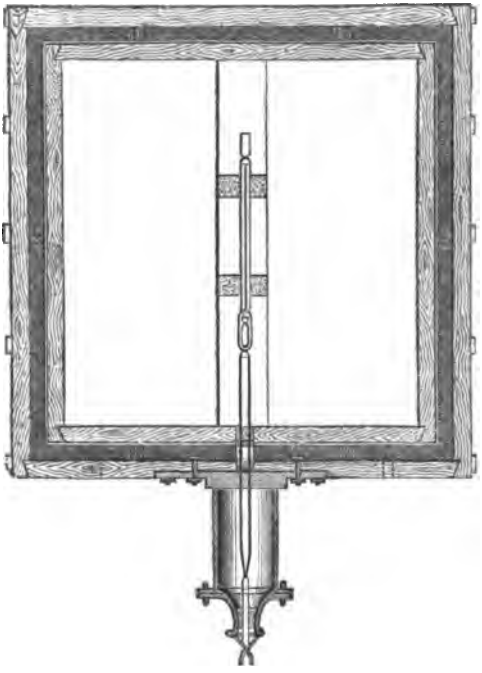
placed, and so destroyed the bridge that what remained of it, presented more the appearance of flax shavings in a confused heap, than of the remains of beams and posts.

EXPERIMENT ON EXPLOSION UNDER WATER.

On Under-water Charges.

A barrel constructed of pine wood, and provided with iron hoops (Fig. 227) was soldered into a zinc-lead drum. This was placed in a second barrel concentrically on a basis of wood, the space between being filled up with pitch. The double electric match pierced the different strata of earth, and every opening was immediately closed up by corks soaked in wax, or gutta-percha laid on warm, or by strips of India-rubber glued over. This explosive barrel lay from the 26th of August, 1859, to the 3rd of April, 1860, in the open sea under water. Its instantaneous ignition on the last-named day, proved how well the method described answered the purpose.

FIG. 227.



EXPERIMENTS ON ENGINEERING WORKS UNDER WATER.

First Experiment: blowing up a Coffer Dam.

A double wall, 24 feet long, was constructed of piles, each made of twenty-six 10-inch pieces 19 feet long, and rammed four feet into the earth (Fig. 228). The distance between the walls was 1½ feet, and the space between filled up with heavy quarry stones (Fig. 229). The heads of

FIG. 228.

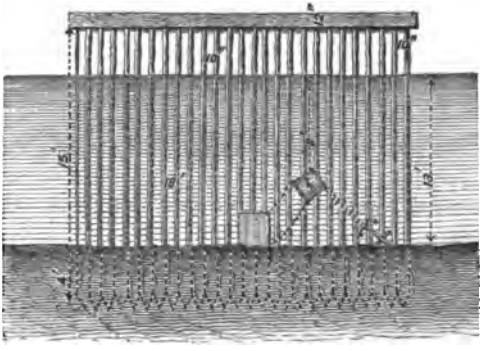
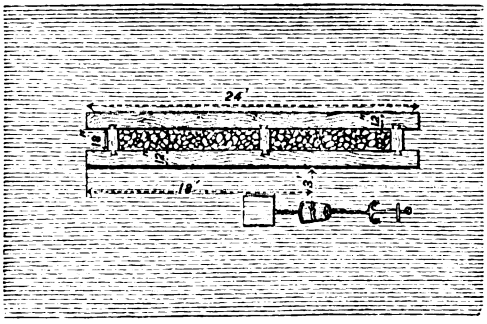
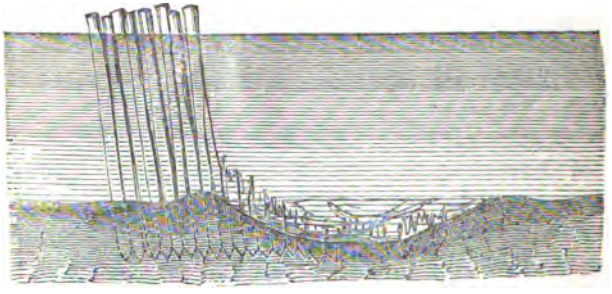


FIG. 229



the piles were tied together by binding sills. The explosive barrel was prevented from floating, by a box filled with stones and by two heavy anchors being suspended from it (Fig. 228). It was sunk 8 feet under water, 3 feet from the wall, and 6 feet from the right, and 18 feet from the left end of it. Two connected pontoons were placed over the barrel. The gun-cotton exploded suddenly and effectually, at the moment when the igniting apparatus was discharged. The surface of the water burst with a hollow sound, and a column of steam and fragments rose to a height of 200 feet. The two pontoons were smashed to pieces; nine of the front piles were left; five piles on the left end of the back wall were loosened and pressed out, and the remaining eight were broken short off at the bottom (Fig. 230). The part filled up with stones had disap-

FIG. 230.

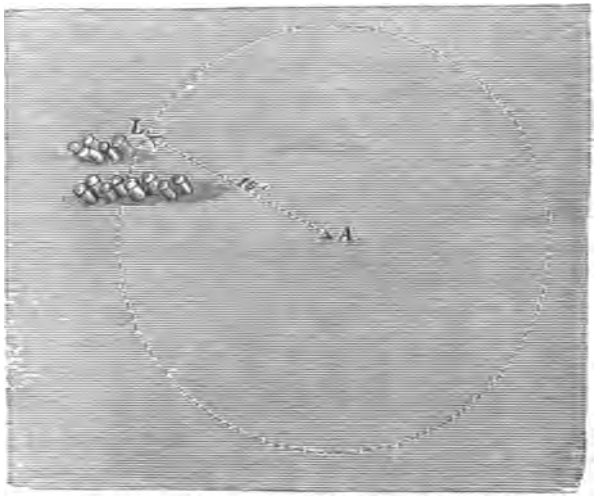


peared, and even the iron anchors were found shattered in pieces.

Fig. 231 shows its condition after the explosion; the radius A, L, of the explosive effect on the horizon of the charge, may be taken at 15 feet. The radius of the action above earth produced by 4 cwt. of gun-cotton under a 2-fathom line of resistance, might

be looked for as 2·88 fathoms. That of the action of the horizon of the charge 3·96 fathoms.

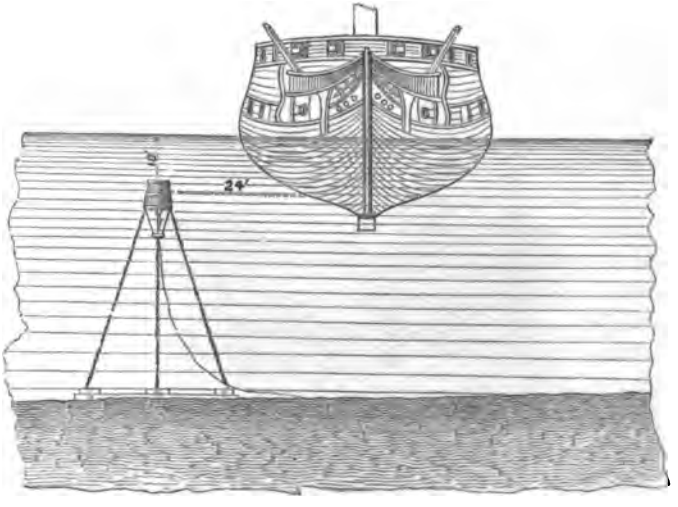
FIG. 231.



EXPERIMENT ON BLOWING UP SHIPS.

A merchant ship, on being blown up with an explosive barre of 4 cwt. of gun-cotton, not only sprang a leak, but was so com-

FIG. 232.



pletely smashed to pieces that it might be safely assumed that such a barrel, whose action extended over more than four fathoms, would be sufficiently powerful to sink a man-of-war struck under the water-line.

Figs. 233 and 234 show the effect of a 25-pound charge of gun-cotton in opening a practicable way through a strong stockade of timber. The experiment was made at Newcastle with the English-made gun-cotton of Messrs. Prentice and Co.

FIG. 233.

FIG. 234.

PYROTECHNY—FIREWORKS.

THIS art, known in Germany under the term of *Die Lustfeuerwerkerei*, and in France as *Les feux colorés*, has long been practised. As the writer of a recent leader in the *Times* says, "even fireworks are no modern conceit. The Chinese, who were the first to discover gunpowder, employed it for this purpose long before they used it for projectiles, and probably centuries before any European nation had learnt to use it at all. Not only squibs and crackers, but fabulous fire-breathing monsters and flying suns letting fall a fiery rain upon earth, rival the most ambitious efforts of English and Parisian artists."

It is also to the Chinese that we are indebted for the beautiful composition still known under the name of "Chinese Fire."

The Florentines are said to be the first European people who gained a knowledge of this art, about the 13th or 14th century. The French followed, having obtained their information from the Italians. The art of making fireworks was afterwards acquired by the English and Germans.

The beauty and ingenuity of Chinese fireworks is thus described by Barrow: "The fireworks, in some particulars, exceeded anything of the kind I had ever seen. In grandeur, magnificence, and variety, they were, I own, inferior to the Chinese fireworks we had seen at Batavia, but infinitely superior in point of novelty, neatness, and ingenuity of contrivance. One piece of machinery I greatly admired; a green chest, five feet square, was hoisted up by a pulley fifty or sixty feet from the ground, the bottom of which was so contrived as then suddenly to fall out, and make way for twenty or thirty strings of lanterns, inclosed in a box, to descend from it, unfolding themselves from one another by degrees, so as at last to form a collection of full five hundred, each having a light of a beautifully coloured flame burning brightly within it. This devolution and development of lanterns were several times repeated, and at every time exhibiting a difference of colour and figure. On each side was a correspondence of smaller boxes, which opened in like manner as the other, and let down an immense net-work of fire, with divisions and compartments of various forms and dimensions, round and square, hexagons, octagons, &c., which shone like the brightest burnished copper,

and flashed like prismatic lightning, with every impulse of the wind. The whole concluded with a volcano or general explosion and discharge of suns and stars, squibs, crackers, rockets, and grenadoes, which involved the gardens for an hour in a cloud of intolerable smoke. The diversity of colour with which the Chinese have the secret of clothing their fire, seems one of the chief merits of their pyrotechny."

In the preceding pages, the principal applications of the two great oxidizing agents, nitrate and chlorate of potash, in the manufacture of gunpowder and lucifer matches, have been given in detail, with a passing notice of the use of the latter salt in the preparation of percussion caps and in heightening the intensity of steam colours. Our present chapter embraces the only remaining technical use of these compounds.

The art of making fireworks, although essentially a chemical one, embraces many mechanical details; the first including the preparation of the materials and their mixture, while the latter consists in constructing the various pieces of apparatus, or devices for exhibiting the chemical action of the former. Advantage is taken of the chemical affinity of the different materials, of the rapid or slow combustion produced by the varying proportions of the ingredients, and of the brilliant colours generated during the burning. The revolving of stars and the flight of rockets &c. are due to mechanical arrangements, and to the resistance or inertia of the air, as the burning material is forcing its way out of a tube.

In the following pages we will shortly describe the preparation of some of the materials and parts of the apparatus used in fireworks, then explain the nature of simple fireworks and those fireworks which are intended for exhibition on the ground, in the air, and on water, with some of the best mixtures for producing coloured flames, &c.

I. PREPARATION OF THE MATERIALS AND APPARATUS.

1. *Materials.*

Nearly all the materials necessary in the preparation of fireworks can be purchased in a form ready for use; those which require a special treatment are the following:—

Zinc.—This metal is used in a state of fine powder, which is easily prepared. The metal is barely melted and poured into a hot mortar, where it is reduced to powder, being kept all the time

at a temperature of 205° C. (401° F.). The whole is then sifted, to remove any particles which have escaped the action of the pestle by the cooling of the metal.

Copper.—This metal is obtained in a state of fine division by precipitating it from a solution of sulphate of copper by means of iron, taking the precaution of using the latter metal in large quantity. The precipitate is well washed, dried between folds of blotting paper, and preserved in well stoppered bottles.

Iron-sand.—A quantity of sulphur is melted in a crucible over a slow fire, and, when it is quite fluid, iron filings are thrown in while the whole is being stirred. The crucible is removed from the fire, and the contents are stirred rapidly till cold. The material is then rolled on a board, till it is broken up as fine as corned powder, after which the sulphur is sifted out.

Soda powder.—This powder is prepared with the same precaution as ordinary gunpowder; the proportions which answer best, being:—

Nitrate of soda	630 parts.
Sulphur	125 „
Charcoal	125 „
	880 parts.

As the nitrate of soda is hygrometric, this powder must be preserved in close vessels from the moisture of the air.

Lead powder.—This mixture is also prepared like gunpowder, and the constituents are used in the following proportions:—

Nitrate of lead	12 parts.
Nitrate of potash	2 „
Charcoal	3 „
	17 parts.

Care must be taken in preparing the mixture upon a large scale to keep it thoroughly moistened, as the mixture of nitrate of lead and charcoal is very liable to ignition by friction.

Prepared Blood.—450 to 500 grammes of zinc are dissolved in 1340 grammes of hydrochloric acid, 22° B., diluted with as much water, and then filtered. This solution is again diluted with its own volume of water, and mixed with fresh blood, The whole is well stirred from time to time for 48 hours, and the clear liquor is siphoned off from the precipitate. The pre-

cipitate is well washed with water, dried, and reduced to powder, in which state it may be kept for any length of time.

2. *Apparatus.*

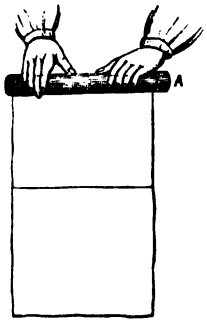
The tools with which the pyrotechnist works, are of a simple character, and consist of formers, drifts, and mallets.

The *Formers* or *Rollers* are of various diameters, depending on the size of the case to be made. Cases are denominated 1 oz., 2 oz., 3 oz., and so on, under the following regulations :—

The 1 oz. case is equal in diameter to a 1 oz. leaden ball, or bullet ; the 2 oz. follows the same rule, and so on for all sizes.

Cases are made to any length, but, according to the above-mentioned rule, should a case 12 inches long be wanted for a Roman candle, we should say a 12 inch case, 1 oz. bore.

FIG. 235.

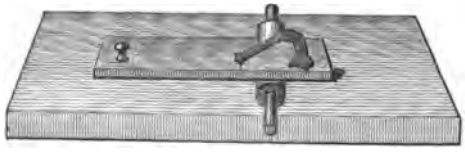


Formers, or Rollers, are made of any hard wood, and in many instances, the blades are covered with brass, or made of solid gun-metal. When made entirely of metal, they do not warp or deviate from truth, which is important where great accuracy is required, and they are easier to work, for the case, when rolled, comes more easily off the roller. They are turned quite straight and very smooth : in Fig. 235, A represents a roller in use.

The *Rolling Table* is generally made of slate, three-quarters of an inch thick, about 28 inches wide, and 3 feet long.

The *Rolling Board* is generally made of yellow deal, about 8 inches wide and 2 feet long. It is fitted with a handle and screw, as shown in Fig. 236.

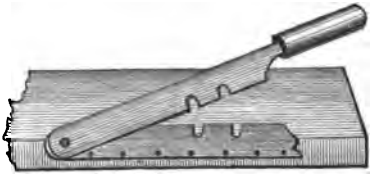
FIG. 236.



The machine for forming a mouth to the case, is called a *Choking machine*, and is made in several ways.

Fig. 237 represents a choking machine, made with two plates of steel with two cuts in each plate ; the bottom plate is fixed on a board, the upper plate works against the lower one by means of a bolt and nut.

FIG. 237.



The case, when about half dry, is placed in one of the cuts of the bottom plate, according to its size, and fits on a peg up to the shoulder. The upper plate is pressed upon it with the right hand, while the left moves the case gently round, so as to form a perfect choke. After several are thus prepared, they are tied with string suited to the size of the case.

3. *Preparation of the Cases.*

The cases are made of cartridge, brown paper, and brown pasteboard. Rocket cases vary in thickness, according to size; and for the convenience of rolling, as well as strength, two or three sheets of brown pasteboard are cut to the proper size and pasted, to go first on the former, after which the thickness is made up with pieces cut out of sheets of 70 lb. Imperial brown paper. The length of the cases is generally 6 or 8 times their diameter. The following are the directions for making the cases:—

Before you begin to roll, fold down one end of your 2-sheet board so far that the fold will go two or three times round the former; take care that the handle of the former is off the table; when you have rolled up the pasteboard, undo about three inches, and in that part which is loose, place a strip of the 70 lb. Imperial and roll it on. Should this make the case too thick, tear off a sheet; or should it not be stout enough, add as much more paper as may be necessary. Having wound the paper on the former thus far by hand, place the case under your rolling board, then push the board forward, which, by repetition, will roll your case very tight, and render it quite firm when dry.

For choking large cases, the treadle machine (Fig. 238) is used. Having rolled your case to fit a mould or knob, now use the choking peg. Push in the nipple about a diameter from the end of the case, taking care that the former shall be a little distance from it. Then give the pinching cord one turn round the case, between the nipple and the former; at first pull easy, and keep moving the case, which will make the neck smooth, and without large wrinkles. When the cases are difficult to choke, let each sheet of paper (except the first and last), in that part where the neck

is to be formed, be slightly moistened with water ; immediately you have struck the concave stroke, bind the neck of the case round with twine, which must not be tied in a knot, but fastened with two or three hitches. The size of the twine must be proportionate to your case ; for 1 oz. cases, fine twine is sufficiently strong, the same for 2 oz. ; ¼ lb. cases require laid cord ; ½ lb. cases, stout laid cord, and so on. Fig. 239 represents a case.

FIG. 238.

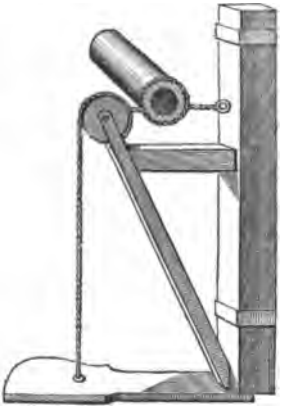
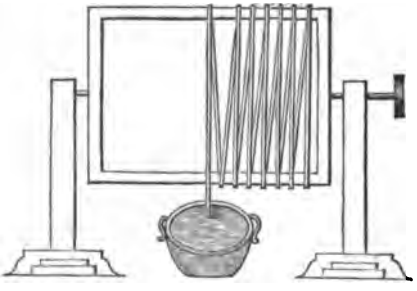


FIG. 239.

4. *Quick-match.*

FIG. 240.



This article is made of cotton wick, which is saturated with a mixture of fine gunpowder and gum made into a thin paste with a little spirits of wine ; or the wicks are boiled with a solution of saltpetre for a few minutes, and then placed in some meal powder. The wick is afterwards stretched on the frame (Fig. 240), well dusted with meal powder, and dried. The following proportions are recommended for the preparation of this match :—

Cotton wick	28 ounces
Nitrate of potash	16 „
Spirits of wine	2 quarts
Water	3 „
Isinglass	3 gills
Meal powder	10 pounds

These wicks are enclosed in paper tubes made in the ordinary way.

The above is an old-fashioned way for manufacturing this article. The present system is as follows:—Obtain 3 lbs. of ball lamp cotton, which is generally wound in two strands; place two of these in a bowl and wind them off into balls of four strands; this will make excellent thin match. When the balls are ready, prepare your gunpowder pulp, which is made in the following manner:—Soak 2 lbs. of the best white gum in cold water for twelve hours; then boil it with six quarts of water; add this gum-paste, and continue stirring it until the whole is well mixed; after which run it through a sieve to prevent any pieces of grit remaining in the gum-water. This being all ready, prepare the gunpowder pulp according to the quantity of match you intend winding on your frames. Say that you will soak down 12 lbs. of F gunpowder: to this quantity pour the gum-water, and continue stirring it with a wooden spatula, until it is of the consistency of thin paste. Now commence laying the four-thread cotton in it, by coiling the same around on the surface of the pulp, continually pressing it down with the back of the hand; when all the cotton is placed in the pulp, let it remain for three hours, then begin to wind it on your frame. When a frame is full, take it off the stand, and place it in the sifting box, to be sifted over with fine meal powder on both sides, after which place the frames out to dry, not in the sun at first, rather in the shade; the next day expose them to the sun's full ray, or in the most sunny situation. This match is generally sufficiently dry in summer-time, two days after it is made. When dry, it will be ready for piping or threading.

The pipes for this match must be made of 16 lbs. yellow-wove double-crown paper, and it must be well sized and tough, possessing a leathery feel with the thumb and four-finger. The papers are rolled on steel wires 2 inches longer than the length of the double-crown sheet. The size of the wire depends on the substance of the match; generally one-third larger answers very

well for almost all purposes. Three of these pipes put together, makes one length, and the match frames are made to suit this arrangement.

5. *Touch-paper.*

This paper is prepared by immersing purple or blue paper in a solution of nitrate of potash in spirits of wine or vinegar, and carefully drying it.

When the touch-paper is used with small articles, a piece is tied round the orifice with thread, leaving sufficient paper to form a small tube at the end. This tube is filled with gunpowder and the paper twisted over it, when all is ready for firing.

Touch paper for capping every description of fireworks, such as squibs, crackers, Roman candles, &c., &c., is prepared in the following manner :—

Dissolve 2 oz. of the best saltpetre in 1 quart of warm water, and take care that the water is very clean. After the mixture has stood for half-an-hour, pour off 1½ pint into a white basin, then cut your sheets of dark blue double-crown paper in half. The weight of the paper should be 12 or 14 lbs. per ream. Place the paper on a slab sufficiently large to give you room to use a small piece of sponge, with which you use the liquor to wet your paper. Cover each half sheet with the liquor as quickly as possible on one side only, and immediately this is done, place it on a line, the wet side outwards ; and when nearly dry, if you have a great number of sheets, place them together as even as possible under a press for one hour, then lay them out to dry, after which they will be quite smooth and ready for use.

In pasting this paper on the work, take care that the paste does not touch that part which is to burn. To use this paper correctly, cut it in strips sufficiently long to go twice round the mouth of the case, or even more if requisite. When you paste on the strips, leave a little above the mouth of the case not pasted ; in small cases, a little meal powder is put into the mouth, and then the paper is twisted to a point. In larger cases, damp priming is used, and when dry, the capping process is proceeded with.

6. *Port-fires*

Are purposely intended to fire the works, their fire being very slow, and the heat of the flame so intense, that, if applied to rockets, leaders, or cases generally, it will fire them immediately.

Port-fires are made of any length, but seldom exceed 21 inches; the interior diameter of port-fire moulds, should be $\frac{12}{16}$th of an inch, and the diameter of the former $\frac{1}{2}$ an inch. The cases must be rolled with paste and one end pinched or turned in, to form a bottom. The moulds should be of gun metal, and take in half or in two pieces lengthways; then, when the case is in, the two sides are held together by rings or hoops, which are made to fit over the outside. The bore of the mould must be made quite through, so that there will be no occasion for a foot. Port-fires, when used, are held in copper or iron sockets, fixed on the end of a long stick. These sockets are made like porte-crayons, only with a screw instead of a ring, but are still better when made with a spring.

FIG. 241.

Port-fires for general use are not charged in a mould; they are made out of demy paper, about 18 lbs. to the ream, and are rolled on formers from $\frac{1}{4}$ to $\frac{5}{8}$ of an inch diameter, and are made from 2 to 8 inches long; they are pinched close at one end, and left open at the other. In filling them, put in a little composition at a time and ram it in firmly, but not hard enough to cripple or break the case. When charged, leave $\frac{1}{4}$ of an inch at the top of the case to receive the priming, which is made with F gunpowder, worked with water to the consistency of putty; or they may be capped with touch paper.

The substance of these cases depends on their size and length, and a few trials will soon make the operator very proficient.

The composition varies according to the intended strength of the fire; and when the fire is to be very slow, it is usual to add some sawdust. The ingredients are sometimes moistened with spirits of wine or linseed oil. The following are some of the mixtures used.

	Government Mixture.									
Saltpetre	6 lb.	pts.	12	8	18	34	8	16	13½	10	11
Sulphur	2 „	„	4	4	10	10	2	8	7½	14	3
Meal-powder	—	„	2	2	24	6	2	—	—	—	—
Fine gunpowder ...	—	„	—	—	—	—	—	—	9	9	12
Fine charcoal	—	„	—	—	—	—	—	3	—	—	—
Green pitch	—	„	—	—	—	—	—	—	—	—	1½
White pitch	—	„	—	—	—	—	—	—	—	—	1½

7. *Leaders, or Pipes of Communication.*

These are small tubes of paper, varying in length with the distances between the fireworks, and filled with a slow burning composition. The rollers for forming these tubes are a quarter of an inch in diameter, and made of brass wire, which is rubbed with an oiled rag previously to rolling the pipes, to prevent the case adhering to the metal.

The placing and joining of these leaders is of great importance in complex fireworks, and the best plan is as follows :—The works being ready to be *clothed* (as this operation is termed), cut the pipes in lengths sufficient to reach from one case to the other, then put in the quick-match, which must go in easily ; when the match is in the tube, cut it off about an inch beyond the pipe, and let it project as much beyond the other end ; then fasten the pipe to the mouth of each case with a pin, and put the loose ends of the match into the mouths of the cases of the works, with a little meal powder ; lastly, paste pieces of paper over the mouths of each, and the joint will be secured.

The leaders must not be placed too near, nor across each other ; and if it cannot be avoided, they must be made very strong and secure at the joints.

II. SINGLE FIREWORKS.

This term is applied to those articles which are distinguished by the simplicity of their construction, and include crackers, squibs, serpents, &c.

1. *Crackers.*

Cartridge paper is employed in the preparation of crackers, which vary in length from 12 to 15 inches, and 3½ inches diameter. One edge of the paper is folded down about ¾ inch in breadth, then the double edge is turned down about ¼ inch, and the single edge is bent back over the double fold, so as to form a channel one quarter of an inch wide. This is filled with meal powder, which is to be then covered by the folds on each side, when the whole is to be pressed very smooth and close, by passing it over the edge of a flat ruler. The part containing the powder is to be gradually folded into the remainder of the paper, each fold being carefully pressed down.

The cracker is then doubled backwards and forwards into as

many folds, of about 2¼ inches, as the paper will allow. The whole is pressed together by means of a wooden vice, a piece of twine is passed twice round the middle across the folds, and the joinings are secured by causing the twine to take a turn round the middle at every turn. One of the ends of the fold may be doubled short under, which will produce an extra report, but the other must project a little beyond the rest, for the priming and capping with the touch-paper. When these crackers are fired, they give a report at every turn of the paper.

The crackers may also be made of two single cards, rolled over each other and covered with paper coated with paste.

The crackers are partially filled with the composition by means of a tin funnel. Ordinary powder is then introduced, and the remaining space is filled with a little sawdust.

The following mixtures are used for ordinary crackers:—

Meal powder . . .	pts.	5	15	6	8	16
Fine charcoal . .	„	1	4	—	2	7
Coarse charcoal . .	„	—	—	6	—	—
Sulphur	„	—	—	2	—	1
Saltpetre	„	—	—	16	1	7

Composition for Crackers with Chinese Fire.

Meal powder	pts.	9	6	16
Saltpetre	„	6	8	—
Sulphur	„	1	2	3
Charcoal	„	1½	1½	2
Fine iron	„	5	—	7
Sand	„	—	5	—

Composition for Crackers with Brilliant Fire.

Meal powder .	pts.	8	8	36	18	32
Sulphur . . .	„	1	1½	1	1	3
Iron filings . .	„	2	2½	—	—	—
Litharge . . .	„	—	—	—	2	—
Steel filings . .	„	—	—	8	3	12

Fig. 242 represents a cracker in section.

Crackers are generally made of elephant or cartridge paper. The cartridge is most in use; and for small-sized crackers a royal cartridge of 20lbs. weight is sufficiently heavy. The following instructions for making crackers are given us by a well-known pyrotechnist:—

Take care to select good coloured paper, and as tough as possible. Cut the paper into strips 3½ inches wide and about 12 inches long, one edge of each fold down lengthwise, about ¾ of an inch broad; then fold the double edges down ¼ of an inch, and turn the single edge back, half over the double fold; then open it, and lay all along the channel which is formed by the folding of the paper, some mealed powder as evenly as possible, then fold it over and over till all the paper is doubled up, rubbing it down every time with a bone folder or burnishing tool; this done, bend it backwards and forwards 2½ inches (with a bone folder or burnishing tool) or thereabouts at a time, as oft as the paper will allow. Then hold all these folds flat and close, and with a small pinching cord give one turn round the middle of the cracker, and pinch it close; then bind it with pack or carpet thread, as tight as you can; then in the place where it was pinched, prime one end of it and cap it with touch-paper. When these crackers are fired, they will give a report at every turn of the paper. If you would have a great number of bounces, you must cut the paper longer, or join them after they are made; but if they are made very long before they are pinched, you must have a piece of wood with a groove in it deep enough to let in half the cracker: this will hold it straight while it is pinching. The woodcuts represent this arrangement:—

FIG. 242.

FIG. 243.

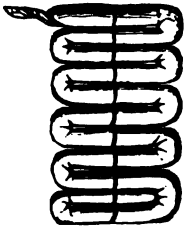


FIG. 244.

Revolving Crackers.

These crackers are charged at each end with clay to a depth of two lines, and filled with a composition without gunpowder. The clay prevents the fire streaming out at the end, and it escapes

through two holes placed opposite each other, as seen in Fig. 245. The two holes are ignited at the same time by connecting them by means of a quick-match, and a rotatory motion is thus communicated to the cylinder, which revolves like a sun.

FIG. 245.

2. *Squibs.*

The cases are made about 6 inches long, by rolling slips of stout cartridge paper three times round a roller, and pasting the last fold. They are firmly tied near the bottom, and made air-tight by sealing-wax, or by dipping the end into hot pitch. They are filled with grained powder or with a mixture of

Gunpowder	8 pts.
Charcoal	1 „
Sulphur	1 „
Steel filings	1 „

which are ground together with a muller or pounded in a mortar. A thimble-full of the powder is put into the case and rammed down hard with a roller, and this is continued until the case is filled. It is then capped with touch-paper, when the squib is ready for use.

The following table contains a collection of mixtures for coloured cases.

Compositions or Mixtures for Coloured Cases.

Materials.	Red.											Rose Red.			Lilac.					Blue.								Green.						White.			Yellow.			Golden Yellow.	Orange Yellow.	Aurora Yellow.						
Chlorate of potash	10	20	9	8	90	10	8	10	8	10	5	48	8	8	20	24	20	146	24	24	26	26	130	26	26	26	8	3	..	80	72	72	72	..	..	..	..	..	..	24	24	24	34	35	124	105	..	..	24	10
Nitrate of potash	..	..	1	2	10	..	2	..	2	..	..	20	2	2	..	..	4	..	..	..	..	..	..	..	..	4	1	..	..	..	..	..	-	..	..	..	..	16	16	32	..	..	..	..	..	..	..	20	..	..	..
Sulphate of potash	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	4	..	..	4	..	1	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Chlorate of soda	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	3	4	..	..
Bicarbonate of soda	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	5	..	5	..	4	3	5	..	..	..	..
Neutral tartrate of soda	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	2	..	..	..	..	..	..	..
Chlorate of baryta	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	12	..	..	..	6	6	5	..	..	..	..	..	..	..	..	..	..	..	2	..	..	..
Nitrate of baryta	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	150	72	100	110	..	1	2	..	..	..	..	..	..	..	..	..	..	..	..	..	10
Sulphate of baryta	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	8	8	8	3	..	..	..	..	..	..	..	3	..
Nitrate of strontia	..	..	..	..	..	..	..	..	..	..	..	72	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Carbonate of strontia	3	6	3	3	30	3	3	3	SO3	Stro	SO3	..	..	3	..	2	3	36	3	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	6	6	30	30	..	..	..
Sulphate of strontia	..	..	..	..	..	..	..	..	3	3	2	..	..	..	..	9	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	5	5	3	3	..	..	..
Oxalate of strontia	..	..	..	..	..	..	..	..	..	..	..	..	..	..	6	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Chalk	..	..	..	..	..	..	..	..	..	..	..	..	3	..	..	..	..	..	3	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Copper powder	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	2	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Sulphide of copper	..	..	..	..	..	..	..	..	..	..	..	5	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	12	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Subsulphate of copper	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	4	..	..	..	..	1	..	3	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Oxichloride of copper	..	..	..	..	..	..	..	..	..	..	..	..	..	..	1	3	2	14	..	2	14	6	70	14	12	10	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Carbonate of copper	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	1	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Nitrate of lead	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	1	..	..	1	..	10	2	2	..	..	..	..	..	..	10	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Chloride of lead	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	1	..	..	1	2	..	..	2	2	..	..	..	60	20	..	..	..	2	1	1	..	..	..	..	..	..	..	..	..	..	..	..
Protochloride of mercury	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	4	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Antimony	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	4	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Sulphide of antimony	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	3	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Red lead	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	1	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Sulphur	..	..	..	..	..	..	..	..	..	..	..	..	..	1	..	3	8	1	8	8	1	1	5	2	1	1	2	1	..	..	1	1	1	..	..	..	7	6	16	2	3	3	1	2	2	3	3	..	3	..
Ordinary gunpowder	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	9	..	..	..	..	..	..	..	..	..	..	..	..	..
Lake resin	2	..	..	2	..	1	..	..	2	2	1	20	2	..	4	3	..	28	..	..	4	4	..	..	4	4	..	2	38	24	24	24	1	1	1	..	..	..	..	..	..	..	..	..	22	..	1	..	3
Colophony	..	3	2	..	12	..	..	..	..	..	..	..	..	1	..	..	..	..	..	..	..	..	12	1	..	..	..	..	..	..	..	..	..	..	..	..	..	..	3	1	6	2	..	12	..	1	3	..
Lac	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	4	..	..	..	..	..	..	..
Pollen of the Pine	..	..	..	..	5	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	5	..	..	..	..	..	..	..	..	..	..	..	..	..	4	..	..	..	..	..	..	..	5	..	..	..	..	..
Prepared blood	..	..	..	..	..	2	..	2	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Nut shells	..	..	..	..	..	..	3	1	..	..	..	..	..	..	..	..	..	..	..	..	..	..	3	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Lamp black	..	..	..	..	..	..	..	..	..	..	..	1	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	1	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
White soap	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	10	..	..	..	..	..	..	10	..	..	..
Cryolite	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	10	..	..

The following are detailed instructions for making squibs :—

The cases are made with 60lb. imperial brown paper and 16lb. white demy; the inside of the case is brown, and the white goes three times round outside. They are rolled in the following manner :—

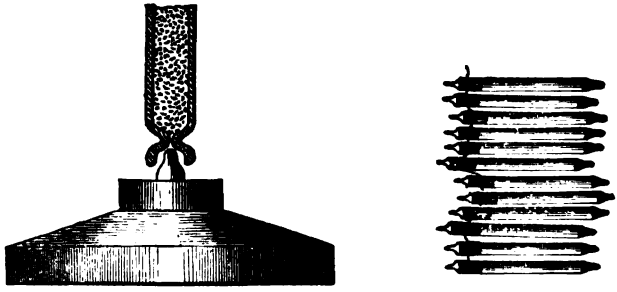
Obtain a brass wire of the size of the serpents; ¼ inch diameter is a useful and good proportion. Cut the brown paper half an inch longer than the white; place the wire upon the brown paper, and commence rolling, till within an inch of the entire length; then place the strip of white, which is pasted on one of the long edges, about half an inch deep; take care to place it as central as possible, and commence rolling it up, when the pasted edge will hold the roll firmly together, forming the case.

The choking is done with the machine previously described.

When the required number of cases are rolled and choked, the charging may commence, which is accomplished with a long funnel and wire.

The case must be placed upon a nipple, Fig. 246.

FIG. 246.



Having charged the case as high as the mark on the wire, take it off the nipple and place it in a clean frame; then proceed with all the cases in the same way. After having charged the whole number, take the cases out of the frame and knock (but very gently) the loose composition, and place them on a wire sieve the meshes of which are sufficiently large to let single F gunpowder pass through easily.

When the sieve is quite full, take a long funnel, filled with single F gunpowder, and hold it over the unchoked end of each

case till it is full; when all are thus filled, knock the sides of the sieve till the grain powder settles down in each case. You now proceed with the closing-in machine, which compresses the ends of the case so firmly as to prevent the slightest fragment of the grain powder leaving the case. After all the cases are closed in, you proceed with the priming and capping. This is done by dipping the choke end in a dish filled with meal powder, taking a properly proportioned slip of touch paper around the mouth of the case about two turns and a half, leaving half an inch for twining; all the cases being thus matched, you take red or white carpet thread in balls, and commence tying the mouth, around the chokes, with two half-hitches until you get a rope of squibs about 18 inches long; cut this off your length of thread, and proceed again, placing the first rope before you in a straight line, the next rope upon it, and so on until all are tied. They may then be packed in dozens, each bundle being secured around the middle of the cases; when all are in bundles, the compressed and pointed end may be dipped into the following composition, technically called "Dip," when the squibs will be complete.

Rosin	4 lb.
Russian tallow	1 „
Turpentine	½ pint.
Venetian red	2 lb.

All this must be melted over a slow fire, and kept stirred until it becomes of the consistency of thick treacle; and the dipping should not be commenced until the unblended colour or drossy matter has settled down.

Another dip is made with 1 lb. of glue to 1 lb. of orange lead of the very finest powder. The glue and red lead are left to soak together in 2 quarts of water for 12 hours; after which it is placed over a slow fire in a large pipkin or tin bowl made expressly for the purpose, the stirring being continued until the whole assumes one colour and appears like a pot of well-mixed paint. When it is boiling hot, 1 gill of turpentine is put into it, and the stirring is continued, after which it is left to settle for 10 minutes, and then the dipping is commenced.

3. *Serpents (or Marroon Squibs).*

FIG. 247.

are a kind of fuzed crackers, 6 to 8 inches long and ½ inch in diameter, sometimes straight and sometimes with a *choke* in the middle, as in Fig. 247. Their name was probably derived from the hissing noise they make, or from the zigzag direction they follow, when fired.

The case being made, and one end tied, it is filled two-thirds up, with a composition of—

Saltpetre	16 parts.
Sulphur	8 „
Fine gunpowder	4 „
Antimony.	1 „

which is rammed down moderately hard. It is then *choked* at B (Fig. 247), leaving a small aperture, and the remainder is filled with grained or corn powder. This end is now well tied with twine and dipped in melted pitch. The other end is opened, and a little damp meal powder is introduced, over which a piece of touch-paper is properly fastened, and the serpent is completed.

4. *Gerbes.*

This firework is made in various ways, generally throwing up a luminous and sparkling jet of fire, somewhat resembling a water-spout: hence its name. Gerbes consist of a straight, cylindrical case, sometimes made with wrought iron (if the gerbe is of large dimensions); but ordinary gerbe cases are made with pasteboard and Imperial brown paper, rendered dense and strong by good rolling and sufficient paste.

Before charging the paper cases, take care to set the inside down upon a nipple, to make the interior quite smooth and free from wrinkles; and, previously to introducing the brilliant composition, put two scoops of first firing or preparatory fire, for which the following will do in cases not larger than ¼ lb. size:—

16 oz. meal powder
6 oz. saltpetre
3 oz. sulphur
3 oz. fine coal.

For larger cases, a less quantity of meal powder will reduce the strength in proportion to the size of the gerbe.

Iron Case Gerbes.

Before putting any composition into these cases, first line them with thin pasteboard, one turn round; after which drive a circular piece of wood a little larger than the diameter of the case (when lined with pasteboard) down upon the neck; you may then commence with a scoop of first firing, after which go on scoop after scoop with the brilliant charge. These gerbes require very solid charging with a heavy mallet, each scoop receiving at least 30 blows; when the gerbe is from a 6lb. upwards, a monkey for charging will be required. After the cases are charged with the brilliant, put in one scoop of clay, and charge this firmly on the brilliant. To complete the gerbe for firing, pass a spoon-bit through the vent and bore a hole through the wood the same size as the vent, to form a proper neck to the case; in this hole you introduce the priming which will ignite the first firing. You may now cap the case with linen or brown paper, to any other material suited to the purpose your gerbe is intended for.

FIG. 248.

Instead of the piece of wood, it is a common practice to charge one scoop of clay into the gerbe before first firing, and beat the clay in the same way as the wooden tampon, and there can be no doubt that this is the better plan.

Gerbe fire for small cases:—

From 2 oz. to 1 lb.
„ 2 oz. to 4 lb.
„ 4 oz. to 1 lb.

Darby's Italian Gerbe.

In addition to this brilliant firework, Mr. Darby has invented an entirely novel and beautiful gerbe, called the Italian or coloured gerbe; they are seldom made larger than ¼lb. size, and rarely less than the 4oz., and require great care in charging. The charge is commenced with gerbe fire, and a scoop of small coloured stars is then introduced, upon which is placed a very small scoop of meal powder; this is gently pressed down with the solid drift, then a scoop of brilliant is introduced, then a

scoop of coloured stars, and so on, till the case is filled. Great care must be taken to set the composition firmly in the case by numerous slight blows with a mallet for 2oz. cases. Should a cascade of these gerbes be intended to finish with a volley of reports, place a 1oz. scoop of single F at the end of each case, and take care to secure them.

Gerbe composition :—

For 2oz. to 8oz. cases.

Meal powder	2 lbs.
Saltpetre	8 oz.
Sulphur	5 „
Fine charcoal	3 „
Prepared iron (No. 1, fine)	24 „

For 8oz. to 1lb. cases.

Saltpetre	2 lbs.
Meal powder	1 „
Sulphur	12 oz.
Fine coal	8 „
Prepared iron (2nd size)	1 lb.

5 *English Pin Wheels.*

Pin, or Catherine wheels are of very simple construction. A long wire about $\frac{1}{16}$ of an inch diameter is the former; on this wire are formed the pipes, which, being filled with composition, are afterwards wound round a small circle of wood, so as to form a helix or spiral line. The cases are generally made of double-crown paper (yellow wove), and cut into strips to give the greatest length, and of width sufficient to roll about four times round the wire, and pasted at the edge so as to bite firmly at the end of the last turn. When a number of pipes are made and perfectly dry, they are filled with composition. These cases are not driven for filling, but are filled by means of a tin funnel with a tube three-quarters of an inch long, made to pass easily into the mouth of the case, which is gradually filled by lifting a wire up and down in this tube, the diameter of the charging wire being half that of the tube. The dry composition being placed in the funnel, the moment an action of the wire takes place, the composition begins to fall into the case, which the charging wire compresses by continuous motion until you have filled the pipe to within $\frac{3}{4}$ of an inch to the top. The pipe

is then removed and the mouth neatly twisted, which will be the point for lighting.

When a number of pipes are ready, place them on a damp floor, or in any damp situation, until they become very pliant, but by no means wet; then commence winding them round a circle of wood whose substance must be equal to the thickness of the diameter of the pipe; and when wound, secure the end with sealing-wax, to prevent its springing open; after winding the required quantity, let them dry. Now cut some strips of crimson or purple paper $\frac{1}{16}$ of an inch wide, and in length twice the diameter of the wheel; then paste all over thoroughly. Take a strip and place it across the wheel diametrically, rub it down, then turn the wheel over, and place the ends down to correspond with the opposite side; when dry, the wheel will be ready for firing.

They may be fired on a large pin and held in the hand, but it is preferable to drive the pin into the end of a stick, which will prevent any accident, should a section of the wheel burst.

6. *Simple Stars or Fireballs*

are generally used in combination with other arrangements, &c., and the composition, of which they are made, consists of—

Saltpetre	16 parts.
Sulphur	8 „
Fine gunpowder	3 „

These materials are mixed with gum and as little spirits of wine as will suffice to make a very stiff paste. This paste is cut up into small squares, which are rolled up into balls on a board covered with gunpowder. The gunpowder which adheres, serves the purpose of firing them. When perfectly dry, they are ready for use.

The French prepare these stars with the above composition in a dry state. A case is made in the usual way, of the dimensions of the intended star, filled with the composition, which is beaten down with a mallet; and the outside being damped, a little gunpowder is sprinkled over it, and the star is complete.

Or, instead of using the gunpowder, a small hole is driven through the centre, and 10 or 12 are strung together on a cotton quick-match, by means of which they can be fired.

Tailed or Cometic Stars.—The ordinary stars are moistened with a mixture of size and spirit of wine, sprinkled with meal

powder. When fired they emit a number of sparks, which represent a tail similar to that of a comet.

Driven Stars.—The liquid used for moistening the composition must be spirit of wine with a little camphor in solution. The cases, containing 1 or 2 ounces, are filled with the moistened composition which is rammed moderately hard. They are then dried, one end is dipped in melted wax, and the other end is damped with spirit of wine, and sprinkled with meal powder.

Stars with Points.—These stars vary in size, from 1 to 16 ounces, and the following are the working instructions for their manufacture:—Roll the case and pinch one end quite close; then drive in half a diameter of clay, and when the case is dry, fill it with composition for 2 or 3 inches of the length of the cases with which it is to burn; at the top of the charge drive some clay; divide the circumference of the case, when full, at the pinched end close to the clay, into five equal parts; then bore five holes with a gimlet about the size of the neck of a common 4 oz. case; into the composition carry a quick-match from the one hole to another, and then secure it with paper. This paper must be put on in a similar way to those on the end of wheel-cases, so that the hollow part which projects from the end of the case may serve to receive a leader from any other work to give fire to the points of the stars.

The following table contains a great variety of compositions for stars.

Materials.	Compositions for Stars.																												Comet Stars.	
	Red.				Crimson.		Violet.		Lilac.		Bright Lilac.		Mauve.				Blue.			Green.		White.		Yellow.						White.	Yellow.
Chlorate of potash ..... pts.	65	42	100	34	25	80	17	115	160	46	168	230	195	65	48	48	22	30	20	35	48	...	...	93	29	29	29	...	...	...
																												NO^3Na		NO^3NaO
Nitrate of potash ..... „	...	...	...	...	...	10	...	...	...	...	...	10	10	...	...	...	...	...	...	...	...	16	76	...	...	...	...	4	100	160
Oxalate of soda ..... „	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	40	8	...	...	...	...	...
Bicarbonate of soda ..... „	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	4	...	...	...
Tartrate of soda ..... „	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	10	...	...	...	...
Sal ammoniac ..... „	...	...	...	...	...	...	2	...	2	7	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Nitrate of strontia ..... „	...	...	...	90	...	80	...	50	...	...	...	80	80	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Carbonate of strontia ..... „	...	...	80	...	...	...	...	...	...	...	...	...	...	...	...	6	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Sulphate of strontia ..... „	46	...	...	...	...	...	...	...	...	...	...	...	...	46	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Nitrate of baryta ..... „	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	60	80	...	...	...	...	...	...	...	...	...
Fluoride of calcium ..... „	...	...	...	...	...	...	...	...	120	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Chalk ..... „	...	15	...	...	9	1	6	...	...	14	43	6	2	...	6	...	...	...	...	...	...	...	...	...	4	4	7	...	...	...
Oxychloride of copper ..... „	...	1	...	...	...	14	...	16	...	8	37	80	35	5	5	3	16	14	16	...	...	...	...	...	...	...	...	...	...	...
Sulphide of copper ..... „	...	...	...	...	3	...	7	40	20	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Precipitated copper powder . „	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	2	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Nitrate of lead ..... „	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	2	...	...	...	...	...	...	...	...	...	...	...
Chloride of lead ..... „	...	...	...	...	...	2	1	...	...	...	...	12	...	...	...	...	...	2	...	...	10	...	...	...	...	...	...	...	...	...
Protochloride of mercury ... „	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	20	...	...	...	...	...	...	...	...	...	...
Sulphide of antimony ..... „	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	2	...	8
Sulphur ..... „	...	18	...	25	10	40	7	70	80	20	75	112	62	...	16	17	8	14	8	20	26	6	34	...	12	12	12	8	25	32
Gunpowder ..... „	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	10	...	...	...	...	...	...	50	...
Charcoal-light ..... „	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	4	...	...	...	...	5	...	...
																														...
Oak charcoal ..... „	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	18	...
Pine charcoal ..... „	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	25	light, heavy
Lamp black ..... „	...	...	...	5	...	5	...	...	...	...	...	5	5	...	...	...	...	...	...	1	2	...	...	...	...	...	...	...	...	15 & 5
Starch ..... „	2	2	3	...	1	4	1	5	9	1	3	8	5	...	...	...	1	1	1	2	3	1	3	4	1	1	1	6	9	...
Resin-lac ..... „	10	...	20	...	...	...	...	...	...	...	...	...	...	10	...	...	...	...	...	2	2	...	...	20	...	...	...	...	...	...
	...	...	...	17	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	28

7. *Sparks.*

These articles differ from stars in size, being very small, and made without cases. The English method of preparing them is as follows:—A mixture of

Fine gunpowder . . . . . 1 part.
Powdered saltpetre . . . . . 3 „
Powdered camphor . . . . . 4 „

is placed in a mortar, and some weak gum-water, in which a little gum-tragacanth has been dissolved, is poured over it, and the whole worked up into a thin paste. Some lint, prepared by boiling it in vinegar or saltpetre, and afterwards dried and unravelled, is placed in the composition so as to absorb the whole. This is then formed into balls about the size of a pea, dried, and sprinkled with fine gunpowder.

In Germany, the following compositions are used:—

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Chlorate of potash .. pts.	24	40	12	20	—	—	—	40	21	21	14	20	96	40
Chlorate of potash and copper ..... „	—	—	—	—	—	—	—	—	23	23	—	—	—	—
Chlorate of baryta .. „	—	—	—	—	18	—	—	—	—	—	—	—	—	—
Nitrate of potash.... „	—	—	—	—	—	12	26	—	—	—	—	—	—	—
Nitrate of lead ..... „	24	—	—	—	—	—	—	—	—	—	—	—	—	—
Nitrate of baryta.... „	—	—	—	40	—	—	—	—	—	—	—	—	—	—
Calomel ..... „	—	—	—	13	7	—	—	28	12	12	4	8	18	—
Sulphide of copper .. „	—	—	—	—	—	—	—	28	—	12	6	4	—	—
Sulphate of strontia . „	—	—	—	—	—	—	—	—	—	—	—	20	72	37
Oxalate of soda .... „	—	16	10	—	—	—	—	—	—	—	—	—	—	—
Chalk ..... „	—	—	—	—	—	—	—	—	—	—	5	—	—	—
Powdered zinc..... „	—	—	—	—	—	14	28	—	—	—	—	—	—	—
Do. charcoal . „	—	—	—	—	—	5	11	—	—	—	—	—	—	—
Sulphur..... „	12	—	1	13	—	—	—	—	—	—	6	3	—	—
Gum-lac ..... „	1	8	—	1	3	—	—	—	—	—	—	2	18	8
Soap ..... „	—	3	1	—	—	—	—	3	3	3	—	—	—	—
Starch ..... „	—	—	—	—	—	—	—	10	—	—	—	—	—	—
Sugar ... . „	—	—	—	—	—	—	—	—	4	4	—	—	—	—
Pine soot ..... „	—	—	—	1	—	—	—	—	—	—	—	—	1	—

The above compositions are intended to give coloured sparks, according to the numbers—

No. 1 gives a bluish white colour.
„ 2 and 3 give yellow.
„ 4 gives green.
„ 5 gives green.
„ 6, 7, 8, 9, and 10 give blue.
„ 11 and 12 give violet.
„ 13 gives red.
„ 14 gives purple.

The materials are mixed with a small quantity of a solution of

starch, so as to form a thick paste, which is forced through a perforated plate, the holes in which are twice as large as it is intended the sparks should be on drying. The small pieces fall on a pasteboard, to which the workman gives a rapid horizontal motion, to round the grains. They are then dried, and those which are perfectly round are selected and separated by sieves of different meshes, to collect those of the same size together.

8. *Roman Candles, or Fire-Pumps.*

These fireworks are made somewhat like gerbes: the cases are cylindrical, and stars are placed between the different layers of the composition. The cases are filled in the usual way with the composition, but in ramming, too much force must not be used, so as to preserve the stars. The stars ought to be flat and circular, and they ought to increase in size, the first being two-thirds of the diameter of the case, and the last fitting tight into the case. The quantity of powder at the bottom of each star must be increased with the diameter of the star.

These candles are placed in rows, some perpendicular and others at various angles, so that the stars may be projected to different distances and directions, to increase the beauty of the effect.

9. *Chinese Fire.*

The principal ingredient of this beautiful composition is the iron-sand; the red and white fire are made as follows:—

Red Chinese or Gerbe Fire.

Calibre of the case.	Saltpetre.	Sulphur.	Charcoal.	Iron-sand 1st order.
12 to 16 lbs.	1 lb.	3 oz.	4 oz.	7 oz.
16 to 22 lbs.	1 lb.	3 oz.	5 oz.	7 oz. 8 drs.
22 to 36 lbs.	1 lb.	4 oz.	6 oz.	8 oz.

White Chinese Fire.

Calibre.	Saltpetre.	Bruised Powder.	Charcoal.	Iron-sand 3rd order.
12 to 16 lbs.	1 lb.	12 oz.	7 oz. 8 drs.	11 oz.
16 to 22 lbs.	1 lb.	11 oz.	8 oz.	11 oz. 8 drs.
22 to 36 lbs.	1 lb.	11 oz.	8 oz. 8 drs.	12 oz.

The iron-sand is moistened with a little spirits of wine and then mixed with the charcoal and saltpetre, which have been previously incorporated in another mortar.

10. *Gold Rain.*

The larger rockets are filled with this firework, which consists of small squares, made in the same way as the simple stars. The following compositions are used :—

	Ordinary.	Chinese.	Composition for immediate use
Saltpetre . . .	pts. 16	4	Saltpetre . . . 4
Sulphur	„ 8	2	Sulphur 2
Fine charcoal . .	„ 2	4	Fine small coals . 1
Pine soot . . .	„ 2	—	Fine gunpowder . 8
Meal powder . .	„ 4	16	Coarse cast-iron . 4

A portion of the cotton is softened in linseed oil, and the materials prepared in a mortar with water.

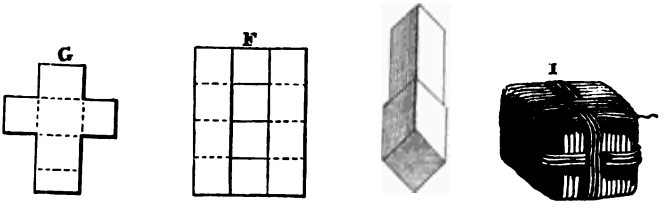
11. *Marroons*

are small cubical boxes, filled with an explosive composition, which explodes suddenly, making a loud report. They are generally used in combination with other fireworks. The boxes are made of pasteboard, the corners being made tight by pasting paper over them, but leaving the top open until they are filled. They are filled with coarse gunpowder, when the top is closed with strong paper well cemented, and the whole box is wrapped round two or three times with lind cord dipped in strong glue. A hole is made in one of the corners, into which a quick-match is introduced, and the marroon is ready for action.

Battery of Marroons.

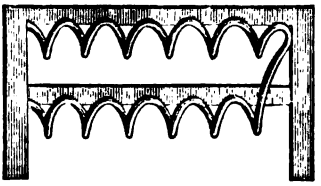
A *Battery of Marroons* may be made by arranging several in various stands, united by cross rails to which they are nailed, and connected by leaders of different lengths.

FIG. 249.



A more simple arrangement is carried out as follows :—Obtain as many hedge stakes as you intend firing, say 21 for a royal

FIG. 250.



salute. Drive a tenpenny nail at the top of each, then drive these stakes in the ground 5 or 6 feet apart, hang a marroon on each, and commence lighting them at one end of the arrangement, taking the required time between the discharge of each marroon. If the marroons are very large, they should be fuzed, and placed at a great distance.

12. *Saucissons.*

These differ from marroons only in form, and till lately, no distinction was made between them, but the French artists have thought proper to give them the above name. The cases of marroons are made cubical, those for the present fireworks are made cylindrical, and must be in proportion about four times their exterior diameter, in length; their diameters may be from one to two and a half or three inches, and the cases increasing in strength as their dimensions.

The cases must be choked or pinched at one end after the manner of rockets, and tied quite close; and afterwards the former on which they are rolled, should be pressed hard upon the bottom, to make it smooth, and to take out the wrinkles left by the choking; the former or interior diameter should not exceed one-half of the exterior diameter of the case. The cases being thus prepared, they are to be filled with coarse powder 1½ diameter high, and the rest of the paper must be folded down tight upon the powder, then bind them tight in every direction, with fine laid cord for small, thick for large; afterwards dip them in the glue;—they are then left to dry. You now cap them with touch-paper or, if large, affix a slow fuze to the mouth of the case; it will then be ready for firing.

Flying saucissons.—These are made in cases, as for ½lb. rockets, vide fig. 251.

Having set down the case, put a small scoop of the following composition:—10 oz. meal powder and 2 oz. fine charcoal, well mixed. After this, charge the case with strong brilliant fire, 2½ diameters high, then pinch the case at the end, using around the choke three half hitches of fine twine; then introduce 1 diameter of F powder; now turn down the inside

FIG. 251.

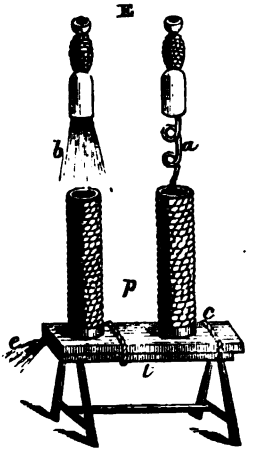


FIG. 252.

paper of the case on the powder, and make the end quite secure; afterwards the marroon portion may be wound with fine laid cord or a stout string, called fine-fine. Then dip this wound portion in one of the dips previously mentioned in this work, and rub the marroon until it appears evenly coated. When quite dry, prime the mouth of the case with damp F powder, taking care to introduce one or two ends of raw quick-match, which will cause certain ignition when the blast of powder is discharged from the saucisson barrel; 1 oz. of gun-powder is sufficient to blow the ½ lb. saucisson high enough to give full effect to its display.

We now pass on to what may be called:—

III. TERRESTRIAL FIREWORKS.

These devices are all prepared by means of the more simple pieces already described. The cases are charged with one of the following mixtures:—

		Common Fire.	Chinese Fire.	Brilliant Fire.
Fine gunpowder . . .	pts.	16	16	16
Fine or coarse coal . .	„	3	—	—
Cast iron	„	—	6	—
Steel turnings	„	—	—	4

Of the innumerable devices which may be manufactured, we can only make the following limited selection.

1. *Suns*

Are either fixed, movable, or transparent. The first are made in the following manner :—A nave of wood has 14 or 16 pieces attached in the form of radii, from which jets of fire proceed, the mouths of the jets being towards the circumference. A match must be applied in such a manner, that the fire, communicated at the centre, shall be conveyed at the same time to the mouths of each of the jets. As they throw their fire, an appearance of a radiating sun is presented, as shown in Fig. 254.

FIG. 253.

FIG. 254.

FIG. 255.

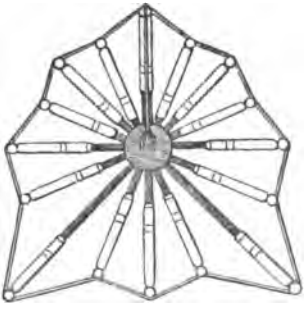
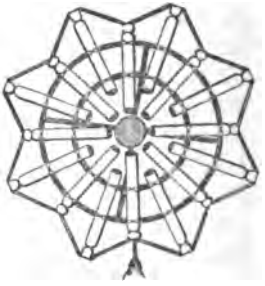


FIG. 256.



When these suns are made with several rows of jets, they are called *Glories*, as seen in Figs. 255 and 256. A fixed sun is represented in Fig. 253.

The sun may also be made to revolve, by attaching jets to it, in the direction of the circumference, with their heads and tails together. These are called turning stars. Two suns with horizontal axes may be placed, one behind the other, and if they are made to revolve in opposite directions, a very pleasing effect is produced by the cross-fire. Again, if each cylinder is charged

with a different mixture, a beautiful variety is produced. The following compositions for the different cases are well adapted for this purpose.

		1 Common Fire.	2 Brilliant Fire.*	3 Flashing Fire.	4 Silver Rain.*	5 Green Fire.	9 Chinese Fire.*
Meal powder . .	pts.	16	16	16	16	16	16
Fine charcoal . .	„	4	—	—	—	—	3
Iron filings . . .	„	—	3	—	—	—	—
Yellow sand . .	„	—	—	2	—	—	—
Saltpetre . . .	„	—	—	—	1	—	8
Steel filings. . .	„	—	—	—	5	—	—
Copper filings . .	„	—	—	—	—	3	—
Fine and coarse cast iron . . .	„	—	—	—	—	—	10
Sulphur	„	—	—	—	1	—	3

Those marked with a * must not be kept more than 10 days, or the brilliancy will be entirely lost.

A revolving sun is represented in Fig. 257.

FIG. 257.

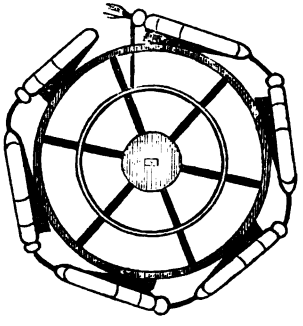
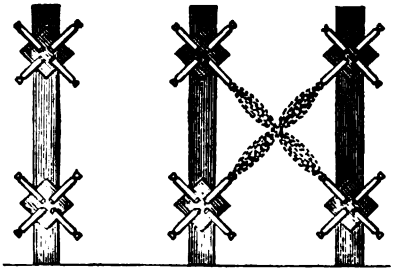


FIG. 258.



A transparent sun is formed in the following manner:—An oiled paper, properly painted, is stretched tight upon a hoop, supported by pieces of strong wire, 6 or 7 inches from the sun, so that the light may illuminate the face. In this way the word *Farewell*, or any other device, may be shown.

2. *Mosaics.*

The length of the flames of the cases must be so regulated that they shall cross each other and unite, as shown in Fig. 258.

A cross may be placed in the centre of each square, which will form a kind of sun. The composition used, is as follows :—

Fine gunpowder	16 parts.
Steel filings	4 „

3. *Palm Tree.*

This device has a similar character, but the leaders must be so applied that each case ignites at the same time. The compositions are the same as those already given, and the character of the arrangements is given in Fig. 259.

FIG. 259.

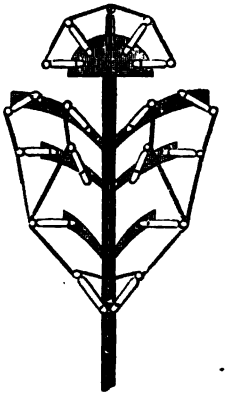
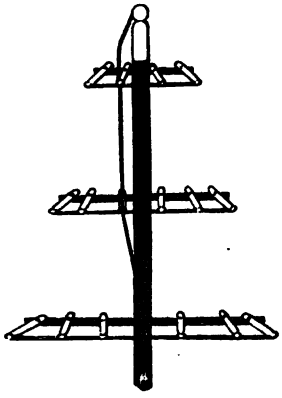


FIG. 260.



4. *Water-fall.*

This device is represented in Fig. 260.

The compositions are the same as before, but for blue fire, the following is recommended.

Fine gunpowder	16 parts.
Saltpetre	8 „
Sulphur	12 „
Zinc filings	12 „

The upper cases must be stronger than those used below, and this device is, of course, susceptible of great variations.

5. *Pièce Pyrique.*

This name has been given to the device in which different fireworks, on the same spindle, are so arranged as to ignite one

after another; they may be either stationary or movable. The ignition of the cases in the stationary *pièce pyrique*, is easily managed by means of the quick-matches, but a different plan is adopted where the parts revolve.

A strong iron spindle, firmly secured to a piece of timber, serves as the shaft to which all the fireworks are attached; these may consist of fixed or revolving stars, as in Figs. 261 and 262; or of branches and twigs, as in Fig. 264; or of a windmill and sails, as in Fig. 263.

FIG. 261.

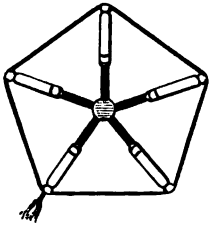
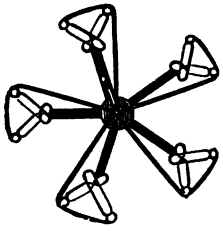


FIG. 262.



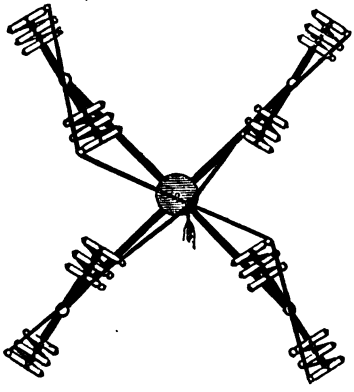


FIG. 263.

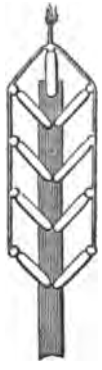


FIG. 264.

FIG. 265.

FIG. 266.

The communication between the fireworks is effected by means of a quick-match leader in a paper tube, and enclosed in a box, as seen in Figs. 265 and 266.

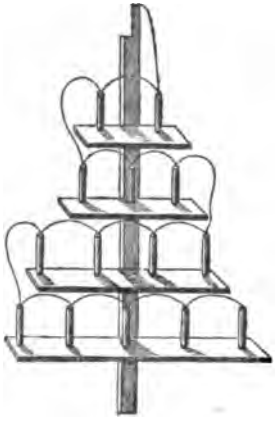
This box is used only in self-mutating pieces. The artist

generally times his mutations, by observation, and applies the port-fire to the leaders accordingly.

In Figure 266 *o p* and *r s* represent two tubes of two fireworks, A and B, each of which ends with a small piece of wick in the open space *q*. This open space is closed by a metal ring, *o o o o*, which prevents any communication from the outside. As one quick-match burns out, the end in the open space communicates the fire to the other, without interfering with the movement of the firework.

6. *Chinese Fountain.*

FIG. 267.



The framework for this device consists of a piece of wood, 6 or 7 feet long by 2½ inches square, on which, about 16 inches below the top, a shelf is fixed, 16 inches long by 2½ inches wide. Several similar shelves are fixed, but each one is 8 inches longer than the one above it. A gerbe is inserted in a hole on the top of the plank, and two gerbes on the first shelf, three gerbes on the second, and so on. The mouths of the gerbes incline forwards, and they are all connected by means of leaders. The top gerbe is first lighted. This device is seen in Fig. 267.

7. *Fixed Fire Globes.*

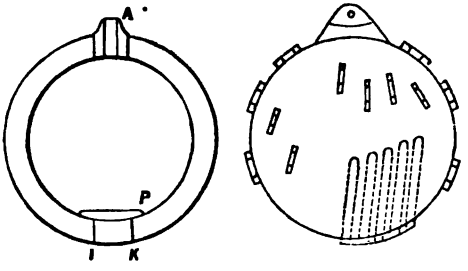
These fireworks are of two kinds, where the cases are either concealed or projecting.

The surface of a spherical ball is divided into fourteen equal parts, and a hole is bored perpendicularly to the centre, in each division. One hole is reserved for the spindle, and all the others are filled with cases containing a brilliant or some other composition. The mouths of the cases are fixed level with the surface of the globe. A groove is cut to connect the mouths of the cases, which are connected by a leader laid in the groove, and these enable the operator to fire all at the same time. When all is dry, the globe is fixed on the spindle, and it is then ready for exhibition.

The other kind of globe is prepared in the same way, but the cases are allowed to project beyond the surface of the globe.

Rolling Fire Globes.

FIG. 268.



A hollow wooden globe is formed, and a small wooden cylinder, A, is inserted, opposite to which there must be a small hole.

The globe is charged with the composition through this hole, and a petard or report of metal, filled with good gunpowder, is placed over the inside of the aperture. Four or five more petards are also inserted, but they do not require to be in metallic cases. The composition for charging the globe is made of

Bruised gunpowder	1 part.
Saltpetre	6 „
Sulphur	3 „
Iron filings	2 „
Greek pitch	½ „

When the globe is fired, by means of a match attached to the orifice A, it begins to roll and leap about, as the petards explode when ignited by the composition. The globes must of course be perforated at various points, otherwise they would burst by the combustion of the composition.

8. *Fire Wheels.*

Every lighted point moving in a circle, as soon as it has acquired a certain velocity, presents to the eye a form which may be called a fire-wheel, and under this definition pastiles, whirlwinds, &c. might all be classed as fire-wheels. The true fire-wheel, however, is so called because it is constructed in the shape of a wheel, with a nave and spokes, and to the extremities of the latter, cases are adjusted, of the rocket species, without heads. The tail of the one is connected with the head of the other, so that when they take fire in succession, a continuous revolution of the apparatus is maintained.

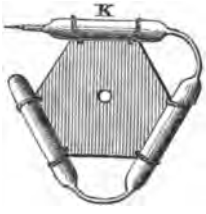
The wheels are either triangular, vertical, or horizontal, and they may be made either single or double.

Single Vertical Wheels.

These wheels may be constructed in a great variety of ways; some have their fells of a circular form, others are hexagonal, octagonal, or decagonal. The spokes are fixed in the nave, the hole in which, is lined with brass, and made to revolve on a smooth iron spindle. A nut is made to screw, on and off, on the end of the spindle, so as to secure the wheel when placed in position. Slips of tin are nailed on, with their edges turned up, so as to form grooves in which the cases lie, when they are tied head to tail.

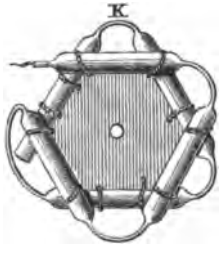
Figures 269, 270 and 271 represent some of the common forms of these wheels.

FIG. 269.



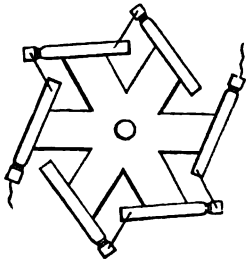
Triangle.

FIG. 270.



Double Triangle.

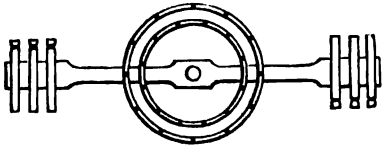
FIG. 271.



Acute Vertical Wheel.

The character of the fire may be varied by filling each case with a different mixture, and the beauty of the whole is much enhanced by the addition of coloured flames, by attaching the cases at right angles on the spokes of the wheel.

FIG. 272.

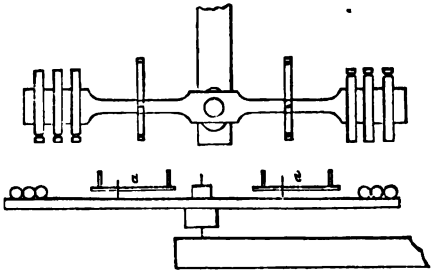


Another description of vertical wheel, which is termed a double radius wheel with illuminated concentric circles, is shown in Fig. 272.

A light strip of wood is used, in the middle of which a nave is inserted. On each end of this piece of wood, three, four, or more cases are fastened, and connected together by matches in such a manner that the one case, as it burns out, ignites another. Stars, suns, and other figures are often fixed on this lath, by which a circular motion is given to the firework.

Another variety is represented in Fig. 273, where two pieces of wood, *a a*, are screwed to the wheel, one arm being longer than the other. A case charged with a flame mixture is fastened at each end, and when the whole is in motion, a series of ever-changing, eccentric circles of flame is produced.

FIG. 273.



Double Vertical or Bisecting Wheels.

A very pretty double wheel is formed as follows:—a light round disk of wood is fitted with a nave in the centre, so that it can revolve on a spindle. Five fountain cases are fastened to the surface, so as to form an angle of 5° with the radius of the disk. They are connected by matches so that all shall begin to burn at the same time. Two wheels, exactly similar, are then fixed on an axle, but made to revolve in opposite directions, when the rays of light cross each other and produce a very fine effect. The number of the cases must not exceed six, and the motion must be slow, to prevent the fire becoming confused.

Plural Wheels

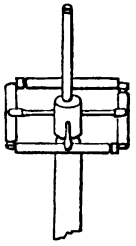
Are so called from the circumstance, that several are fixed on the same axis. They are generally horizontal, and consist of three sets of spokes, six being fixed at the top, six at the bottom, and four in the middle.

The cases must be fixed to the ends of the spokes in grooves cut for this purpose, or half-cylinders of tin may be nailed to the ends of the spokes, and the cases tied in them. In clothing these wheels, the upper set of cases plays obliquely downwards, the middle set, horizontally, and the bottom, obliquely upwards. The leaders must be so arranged that the cases shall burn, first up, then down, then horizontally, through all the sets. If two or three ladles of slow-fire are driven in the end of the last case, it will burn till the wheel stops, and if the other cases are fixed in the contrary direction, the motion of the wheel will be reversed, and present a pleasing effect.

Horizontal Wheels.

A wheel with nave, spindle, and spokes is fitted with a circular fell, which may be formed with a broad cooper's hoop. A piece of wood with a groove, to receive the case, is nailed to the end of each of the four to eight spokes, and they are so arranged that half the cases incline up and down, while the heads and tails approach each other. A leader connects the mouth of one case

FIG. 274.

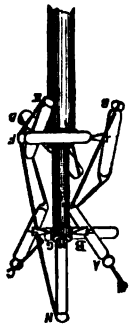


with the tail of another, when the cases will take fire in succession, one burning upwards and another downwards. A case of Chinese fire may be placed in the middle to burn as long as two or three of the cases on the wheel.

Horizontal wheels are often fired two at a time, and made to keep time with the vertical wheels.

Caprice and Furilona Wheels.

FIG. 275.



These are horizontal wheels, the cases on which are so arranged, that they turn and turn about, sending their fire upwards and then downwards.

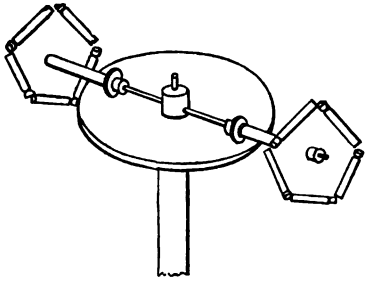
The firework consists of a centre piece, A (Fig. 27)5, which rests on a fixed upright support, and which can easily revolve. Two small arms or spokes, B, are attached to it, and the cases are placed on these arms. It is important to attend to the position of the cases, as shown in the figure. The cases, *a*, *b*, *c*, *d*, ignite in succession, and are followed at last by those marked *e*, *f*, *g*, *h*, which all take fire at the same moment, forming a fir tree, which concludes the display.

Spiral Wheels.

This device may be either single or double, and in the latter case, the nave must be as long as the height of the spiral lines. The spokes fixed in the nave, diminish in length from the wheel to the top, as in Fig, 276. The worms are nailed to the spokes, and the worms are closed with illuminations. The top may terminate in a fire-sheaf, a case of spur-fire, or an amber light.

FIG. 276.

FIG. 277.



These spiral wheels may be illuminated in a variety of ways.

Plate Wheel or Table Piece.

This firework is made by screwing two round iron arms into an upright nave, which revolves with the arms on a spindle. A fire wheel with four or five cases is then attached to the outer end of each arm, on which a roller is fixed, resting on a wooden circular plate, whence the name, as shown in Fig. 277.

This wheel is said to combine the two kinds, vertical and horizontal, already described.

Balloon Wheels.

These are horizontal wheels, in which pots are arranged to correspond with the cases. A small opening is made in the bottom of each pot, into which a leader is carried from the tail of each case. The pots are charged with stars, crackers, serpents,

&c., and as the wheel turns, the pots are fired in succession, throwing a great variety of fires into the air.

9. *Pastiles or Pinwheels.*

These pyrotechnic arrangements were formerly called *Table Fireworks*, and are really a kind of small suns, the long paper cases of which are rolled spirally on a rocket stick, or a wooden rod with a hole in the middle, and charged with a quick firing composition. They approach the character of wheels, but they last longer and revolve much more rapidly, producing very beautiful effects.

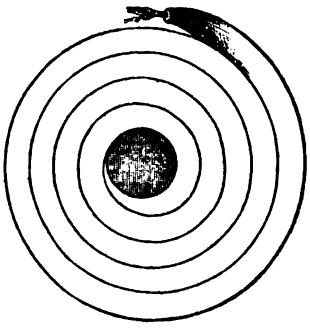
The cases require great care in their preparation, and the paper must be of good quality and well glued, but the details of their manufacture are similar to those already given.

The charge must not contain any large grains, and is always sifted to remove the coarser particles. When the cases are charged and finished, they are passed under rollers, and the surface of the case is afterwards coated with a solution of gum or good paste.

The character of the charge varies with the object of the artist. The following table contains some of the most approved mixtures.

The appearance of the pastile is shown in Fig. 278.

FIG. 278.



A pin without its head, firmly inserted into the end of a small stick, serves as the pivot on which the pastile turns, and the charge is ignited with the ordinary precautions.

The foreign pastile works horizontally, but those made in this country move in a vertical direction.

Dahlia Pastiles.

This modification is the invention of Chertier, and consists of two different kinds of pastiles fixed on the same spindle, one of the ordinary character and the other charged with alternate mixtures of different coloured fires.

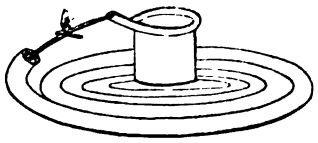
The case for the latter is made of thin sheets of paper, one side of which is brushed with a strong solution of nitre, and the formation of the case is completed in the usual way. The dif-

Compositions for Simple and Coloured Pastiles.

	Simple.															Coloured.						
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	Red.	Lilac.		Blue.	Green.	White.	Yellow.
Ordinary gunpowder... pts.	16	9	32	16	9	9	...	..	32	8	...	...	...	...	...	...	...	...	...	...	...	...
Soda do. ... ,,	...	...	...	...	...	...	18	18	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Lead do. ... ,,	...	...	...	...	...	...	...	...	...	...	17	34	34	17	34	...	...	...	...	...	...	...
Nitrate of potash ..... ,,	...	4	4	1	4	4	9	9	1	...	...	...	...	...	...	..	...	...	...	...	...	...
Sulphide of antimony , ,,	...	...	5	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Litharge .... ,,	1	...	...	...	...	...	...	...	...	...	...	...	...	...	..	...	...	...	...	...	...	...
Varnished filings ..... ,,	...	...	...	...	1	...	...	2	...	...	plain 8	plain 5	5	...	...	...	...	...	...	...	...	...
Brass do. ..... ,,	...	...	...	...	...	1	...	...	...	1	...	...	...	...	5	...	...	...	...	...	...	...
Steel do. ..... ,,	...	...	...	...	...	...	...	...	4	...	...	...	1	...	...	...	...	...	...	...	...	...
Varnished zinc powder ,,	...	...	...	...	..	...	...	...	...	6	...	...	...	...	...	...	...	...	...	...	...	...
Cast-iron filings..... ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	2	...	...	...	...	...	...	...	...
Charcoal ..... ,,	...	...	...	..	...	...	1	1	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Mica ..... ,,	...	...	...	2	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Nitrate of baryta ..... ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	75	...	...
Chloride of lead..... ,,	...	...	...	..	...	...	...	...	...	...	...	...	...	...	...	...	...	...	1	20	...	...
Oxychloride of copper . ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	2	6	...	...	...
Copper in powder ..... ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	2	...	...	...	...	...
Bichromate of potash . ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	3	...
Carbonate of strontia . ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	3	3	...	...	...	...	...
Chalk ..... ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	3	...	...	...	...
Lake resin .... ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	2	...	...	...	25	...	...
Sulphur ..... ,,	...	1	...	...	1	1	2	2	1	...	...	...	...	...	...	...	8	8	5	1	8	1
Chlorate of potash..... ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	10	24	24	12	70	24	4
Oxalate of soda ..... ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	2

ferent charges are added, one after another, according to the taste of the artist. The case is then rolled and beaten to the required curve by means of a leather strap.

FIG. 279.



The ordinary pastile is immovable, but that containing the coloured fires revolves on a strong needle, as already explained.

The appearance presented by this double pastile is seen in Fig. 279.

Chertier has improved this pastile by adding an arrangement for furnishing coloured fire rain.

10. *Bengal Lights.*

This device consists in filling small saucers with any of the charges in the following table; and small pieces of wick are placed on the surface. A double wick is fixed in the centre, and the saucers are then covered with strong paper, which is securely glued to the edge. The wick in the centre is passed through the paper cover and placed in communication with other saucers, by means of ordinary connecting tubes. The ignition is made by means of a lighted taper.

Another plan consists in using a case made of thick paper, which is filled with the charge slightly damped, and gently beaten with a cylinder. The outer surface of the case is coated with gum, to prevent the fire travelling down the side. These cylinders being suspended in rows near any object to be illuminated, and ignited, will produce a beautiful effect.

11. *Theatre Fire.*

The compositions used for these fires often contain sulphur, which, when burnt, produces sulphurous acid, to the annoyance of both the performers and the audience; antimony, realgar, calomel, are also often present, which, being volatile, exert an injurious action on the health of the parties present.

Compositions for Bengal Lights.

Materials.	Red.	Crimson.	Rose Red.			Lilac.				Violet.	Blue.				Green.					White.		Yellow.							Purple Orange.
Chlorate of potash..... pts.	72	15	9	19	18	45	85	17	26	26	64	40	33	64	20	6	9	...	...	...	...	12	10	5	8	...	18	12	16
Chlorate of baryta..... ,,	...	...	...	...	...	...	...	...	...	...	..	...	...	...	...	...	...	12	20	...	...	...	...	...	...	...	...	...	...
Nitrate of potash ..... ,,	...	...	2	...	20	23	10	2	...	...	...	...	...	...	...	...	...	...	...	32	5	...	...	...	...	...	...	...	...
Nitrate of soda ..... ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	16	...	12	...
Nitrate of baryta ..... ,,	...	...	...	26	...	...	10	2	...	...	20	10	20	20	80	40	27	...	15	...	...	24	12	6	24	...	...	...	...
Nitrate of strontia..... ,,	450	29	...	36	36	...	...	...	36	36	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	90	90	90
Sulphate of potash..... ,,	...	...	...	5	3	...	8	2	9	10	15	8	10	17	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Bicarbonate of soda ... ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	4	2	1	...	...	...	...	...
Oxalate of soda ..... ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	12	...	6
Carbonate of strontia . ,,	...	...	...	...	...	...	...	3	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	1	5	...	...	...	...
Chalk ..... ,,	...	...	3	...	...	2	15	...	...	...	...	...	...	...	...	...	...	...	...	...	...	1	2	...	...	...	...	...	...
Chloride of ammonium ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	4	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Chloride of lead..... ,,	...	2	...	2	...	...	...	...	...	...	2	1	1	2	...	...	2	...	...	...	...	...	...	...	...	...	...	...	...
Sulphide of copper ... ,,	...	10	...	...	...	5	...	...	...	...	...	...	...	...	1	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Subsulphate of copper. ,,	...	...	...	3	3	10	12	...	9	...	20	12	10	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Sulphide of antimony . ,,	...	...	...	...	4	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	1	...	...	...	...	6	...	...	...
Chloride of copper ... ,,	...	...	...	...	...	...	...	2	...	8	...	...	...	18	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Protochloride of mercury,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	11	...	5	8	...	...	...	...	...	...	...	...	...	...
Antimony ..... ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	12	...	...	...	...	...	...	...	...	...
Minium ..... ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	10	...	...	...	...	...	5	...	...	...
Sulphur ..... ,,	125	13	...	24	24	20	17	3	28	28	33	17	23	33	26	8	8	..	6	15	2	8	4	2	8	7	25	25	25
Lamp black ..... ,,	25	...	...	2	2	...	...	...	2	2	...	...	...	...	2	2	...	...	...	...	...	...	...	...	...	...	5	5	5
Lake resin ..... ,,	...	1	2	...	...	...	10	2	...	...	...	...	3	...	2	1	2	2	1	...	...	...	1	...	...	...	...	...	...
Colophony ..... ,,	...	...	...	2	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	2	1	1	2	...	...	...	...
Starch..... ,,	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	1	...	...	...	...	...	...	...	...	...

The following compositions are free from both of these objections:—

Materials.	White.	Yellow.	Green.	Red.
Chlorate of potash . . .	12	6	2	12
Nitrate of potash	4	6	—	4
Nitrate of baryta	—	—	1	—
Carbonate of baryta . . .	1	—	—	—
Oxalate of soda	—	5	—	—
Oxalate of strontia . . .	—	—	—	1
Lacture	4	—	1	4
Stearin	1	—	—	—
Shellac	—	3	—	—
Lycopodiun	—	—	—	1

These compositions are prepared in the usual manner and filled into cases similar to those used for Bengal lights.

The flame of alcohol, coloured with some material, is also often used in theatres. A piece of unspun cotton is dusted with the dry composition and made up into a ball. This is placed in a saucer and ordinary spirits of wine poured over it, another portion being added as the first burns off.

Another arrangement consists in employing a round tin box, 4 inches deep and 4 inches in diameter. A round hole, 1 inch in diameter, is made in the lid, into which a tin tube, pierced with holes, is fixed. A cotton wick to fill this tin tube, is steeped in an aqueous solution of the colouring agent, and then dried. The box is filled with the spirits of wine, the wick is inserted in the tube, and then ignited.

The different colours are obtained by using the following materials:—

Yellow.—Nitrate of soda.

Red.—Chloride of strontium.

Green.—Nitrate or iodide of copper, and boracic acid.

Chloride of copper colours the flame green, which changes to *blue* at those points where the wick is not completely saturated with the alcohol.

Blue.—A little pure nitrate of potash.

IV. ATMOSPHERIC FIREWORKS.

We will describe in this chapter those fireworks which have their characteristic action in the air; and foremost among all these devices, stands the rocket.

1. *Rocket.*

This pyrotechnic instrument is called *Rakete* by the Germans, *Rochette* by the Italians, and *Fusée volante* by the French.

Rockets have been known from an early period, and the first account which has been discovered, is found in the works of Marcus Græcus, mentioned by an Arabian physician, called Mesue, who lived about the 9th century. Among several ways of meeting an enemy, the following details are given, amounting to a clear description of a rocket:—"Mix together one pound of live sulphur, two of charcoal of willow, and six of saltpetre, reducing them to a very fine powder in a marble mortar. A certain quantity of this is to be put into a long, narrow and well compacted cover, and discharged into the air."

Rockets were also prepared during the reign of the Emperor Leo, about A. D. 880, and have been known in China, India, and Persia from time immemorial.

It is to General Desaguliers that we are indebted for the idea of using rockets as engines of war. He was not successful in reducing his idea to practice, which was taken up by Sir W. Congreve, and by him it was rendered an effective weapon of attack. Various improvements have been introduced, of which notice will be taken in the following details of the manufacture of the rocket.

FIG. 280.

Rockets consist of strong paper cylinders filled with the composition, which is rammed hard. When fire is applied to the opening, they fly in any given direction. A head is generally fixed at the one end, which contains corn-powder, sparks, and other decorations, and when the rocket is consumed, these ignite, burst in the air, and produce the well-known beautiful appearance of the *Sky-rocket.* Some are made to run along a line, and are hence called *Line-rockets or Courantines,* while others are fixed on the circumference or axle of a wheel, and are then designated *Wheel-rockets.*

The principle of the rocket is the same, however much it may change its appearance, whether it carry ornamental fireworks, or shot, shell, or carcasses, as in the congreve rocket. The course of the rocket is regulated by attaching a long stick to serve as a guide. The principle of the rocket is shown in an excellent woodcut (Fig. 280) which we

copy from Scoffern's interesting volume "The Projectile Weapons of War," in which A represents the paper cone, in order to facilitate its passage through the air; B, the chamber which contains the bursting powder and the ornamental fireworks; C is a layer of clay, wood, paper, &c., perforated with a hole, to allow the fire to reach the composition D; E is a hollow conoidal cavity to effect a rapid combustion; and F is the guiding stick, attached to the rocket by wire or cord.

With this general description of the principle of the rocket, the following details will be more intelligible.

Sky-rocket.

The relative magnitude of rockets is estimated by the diameter of the lead balls or bullets, upon which their orifice is fitted; thus there are three kinds, viz., those whose internal diameter does not exceed that of a pound bullet, called *Small-sized Rockets;* those, whose calibre varies from one to three pounds, are termed *Middle-sized Rockets;* and those above these dimensions, are the *Large-sized Rockets.*

They are made according to the following proportions:—taking the diameter of the orifice, the height should be equal to six diameters and two-thirds, and the choke must be one diameter and one-third of this model; thus, supposing the diameter of a 1 lb. rocket to be $1\frac{1}{4}$ inch, and multiplying it by $6\frac{2}{3}$, the length of the case must be $10\frac{1}{3}$ inches, and the choke $2\frac{1}{4}$ inches.

FIG. 281.

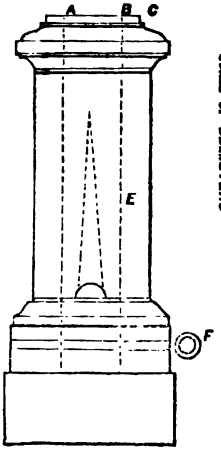
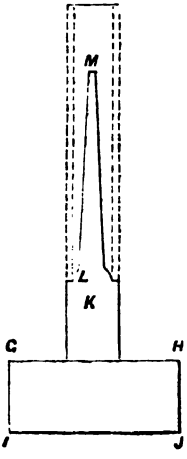


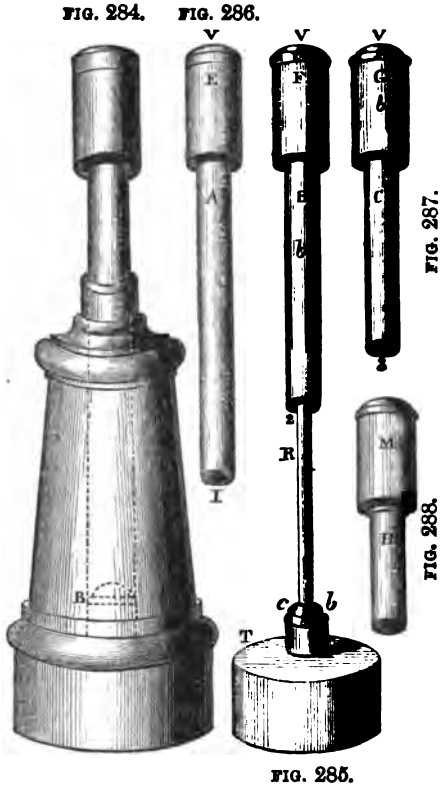
FIG. 282.

FIG. 283.



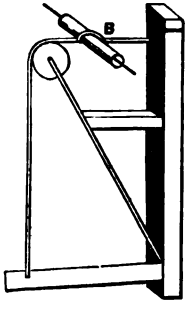
The moulds employed in making rockets are represented in Figures 281 and 283. They are constructed in proportion to the diameter of the calibre, and divided into a scale of equal parts. A B is the calibre or diameter, and C D the height; E is the thickness of the mould, and F an iron pin, by which the cylinder is firmly secured to the foot. Fig. 283

represents the foot detached from the cylinder. G, H, I, J, is the base, and K, the choke, which connects the cylinder and foot; L is the nipple, and M is called the piercer, which is formed of iron. Fig. 285 is a former in two pieces connected with a pin, both ends being rounded off, so that the choke or contraction in the cartridge may be more easily managed. Figs. 286, 287 and 288 are *rammers* or *drifts* used in loading the cases, and they must be pierced lengthways to fit on to the piercer. Fig. 284 represents the mould with the rammers, &c. all complete.



The cases for small rockets are made of cartridge-paper, and those for larger sizes, are constructed of pasteboard The mode of making them is similar to that previously described, and the contraction or choke is effected by the apparatus shown in Fig. 289. The former is joined by means of the connecting wire, and the cord is passed once round the case, exactly over the junction of the two, when the treadle is gently pressed, while the case is kept rolling on the line.

FIG. 289.



The case is now inserted in the mould without the foot, and placed on a solid block, when the former is driven hard upon its end piece. The case is then cut to the proper length, allowing it to rise a little above the mould. The former is now withdrawn and

the case is replaced in the mould, with the foot and piercer properly attached, when it is driven down upon the piercer with the long perforated rammer, called a *setting down drift.*

The filling and ramming of the cases requires great care and attention, in order that the rocket may rise to its proper height with a uniform motion. The composition must not be too dry, and not more than one diameter in height, should be added at one time. The rammer should be kept turning round in the case while the composition is being beaten firm and compact. After each addition has been rammed hard, the cartridge must be inverted, to allow the loose particles to fall out. The apparatus must be placed on a solid block, and the mallets must be in proportion to the size of the rocket.

The cartridge being filled as high as one diameter above the piercer, half the folds are turned back on the composition, and then pressed down with a rod and mallet to make them smooth. Three or four holes are then pierced through the folded paper down to the composition, so that there may be a communication between the charge and the empty space at the extremity. This empty space in small rockets, is filled with granulated powder, and is covered with paper, which is either pinched quite close by means of the choking apparatus, or crowned with a conical cap. This space in larger rockets, is filled with pots containing the stars, serpents, rockets, gold and silver rains, &c., &c.

The last arrangement is to fix the rocket to its rod. The length of the rod or stick depends on the size of the rocket, thus, for rockets of—

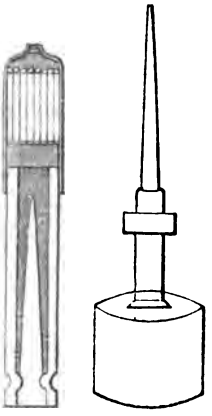
6 lbs.,	the stick must be	14	feet	10	inches long.
4 „	do.	12	„	10	do.
2 „	do.	9	„	4	do.
1 „	do.	8	„	2	do.
8 oz.	do.	6	„	6	do.
4 „	do.	5	„	3	do.

The top of the stick must be level with the head of the rocket, which must be secured by cord near the top of the stick, and again at the neck of the rocket.

These sticks are usually straight, and cause the rocket to ascend in a straight line; but if the rod is curved, the motion of the rocket is inclined in the direction of the bend of the stick; the centre of gravity then draws it afterwards towards a vertical position, and this alternate action gives a spiral form to the ascent which produces a pleasing effect.

The motion of the rocket can also be varied in another way by the following arrangement :—a small round piece of sheet tin, about 3 or 4 inches in diameter, is fixed under the mouth of the case, about 16 inches from the neck of the rocket, upon a wooden bracket, and when the rocket ascends, the fire plays with greater force on the tin, dividing the tail in such a manner that it forms an arch as it mounts in the air.

FIG. 290.



The apparatus used in Germany for making rockets is shown in Fig. 290. The previous description applies to this apparatus, which requires no further explanation.

The following tables contain the mixtures of materials for rocket compositions, as employed in this country and in Germany.

Charges for Rockets.

Size.	Meal Powder.		Saltpetre.		Charcoal.		Sulphur.		Steel-Filings.	
	lb.	oz.	lb.	oz.	lb.	oz.	lb.	oz.	lb.	oz.
Rockets of 4 oz.	1	4	0	4	0	2	...		...	
Do. 8 oz.	1	0	0	4	0	1½	0	8	...	
Do. 1 lb.	2	0	0	8	0	2	0	4	0	1½
Sky-rockets in general.....	0	2	4	0	1	12	1½	0½	...	
Do. large	1	0	4	0	...		1	0	...	
Do. middle-sized	1	0	3	0	1	0	2	0	...	

Rocket Stars.

Colour or character.	Meal Powder	Saltpetre		Sulphur.	Camphor.	Oil of Spike.	Spirits of Wine.	Antimony.	Isinglass.	Oil of Turpentine.	Charcoal coarsely ground.
	oz.	lb.	oz.	oz.	oz.	oz.	oz.	oz.	oz.	oz.	oz.
White stars.....	4	0	12	6	5	2	...	...	...	...	...
Blue stars	8	0	4	2	...	2	2	...	...	...	...
Variegated stars	3½	0	4	2	2	...	...	...	...	...	...
Brilliant stars...	0¾	0	8½	1½	...	...	...	...	...	...	...
Common stars .	...	1	0	4	0¼	...	0½	4¾	0½	...	...
Tailed stars ...	2	0	2	2	...	...	...	...	...	...	0¾
Stars of a fine colour	1	0	1	1	0¼	...	...	...	...	0¼	...

Rains for Sky-Rockets.

Character.	Sawdust.	Sulphur.	Glass Dust.	Antimony.	Brass Dust.	Saltpetre.	Charcoal.	Steel Dust.
	oz.	oz.	oz.	oz.	oz.	oz.	oz.	oz.
Gold rain	0¼	2	1	0¼	0¼	8	...	...
Silver rain	...	2	...	...	...	8	4	0¼

German Composition for Rockets.

Character of Fire.	Saltpetre.	Coarse Charcoal.	Sulphur.	Meal Powder.	Coarse Metal Filings.	Iron Filings	Glass, broken.	Sand, moistened.	Charcoal.
Ordinary fire	16	7	4	..	...	...	...	...	...
Chinese fire, No. 1	16	8	4	8	8	...	...	...	...
Do. No. 2	16	...	7½	12	...	...	...	11	...
Brilliant fire, No. 1	4	...	...	16	...	1½	...	...	4
Do. No. 2	1	...	...	4	...	...	0½	...	1
Do. No. 3	2	...	...	8	...	...	1	...	2

Towering Rockets.

When one rocket is fixed on the top of another of larger dimensions, they are called *Towering Rockets*, as they ascend to a greater height. A head without a collar is fixed on a pound rocket, for example, and the mouth of a four-ounce rocket is rubbed with meal powder, moistened with spirits of wine, which is placed in the head of a large rocket with its mouth downward, while a piece of quick-match is fixed in the hole of the clay of the one-pound rocket. This match must be long enough to go a short way up the bore of the small rocket, in order to ignite it when the large rocket is burnt out. A little tow must be rolled round the four-ounce rocket, in order to fill the head of the other, in which it will then stand in an upright position. A single paper is then pasted round the opening of the top of the head of the large rocket, and the stick for such rockets must be a little longer than for those headed with stars, &c.

Honorary Rockets.

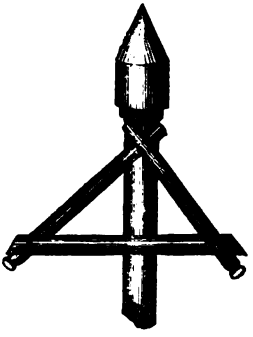
These are similar to sky-rockets, with the exception that they carry no head nor report, but are closed at the top, on which a

cone is fixed. A 2 oz. case, about 5 or 6 inches long, filled with a strong charge, pinched close on both ends, is tied on the case, close to the top of the stick. A hole is bored in the reverse side at each end, and a leader from each hole is carried to the top of the rocket. When the rocket is fired, and arrives at its proper height, the case at the top is ignited, which causes both the rocket and the stick to revolve rapidly, on their return, representing a worm of fire descending to the ground.

Caduceous Rockets.

This name has been given to these rockets from their resemblance to the rod carried by Mercury, which was entwisted by two serpents, as the sign of his office, and hence called by the Germans *Merkurstab*. This term, *Caduce*, was applied by the Romans to a similar staff or wand, which was carried by the officers who went to proclaim peace to the enemy.

FIG. 291.



If two rockets are fixed obliquely on the opposite sides of a rod, they will form two spiral lines in their flight; but they must exactly balance each other, to render the ascent perfectly vertical.

The two ends of the rockets are choked close, without head or bounce, and the rods ought to be square. The mouths of the rockets must be connected by a leader, which, when they are fired, must be burnt through the middle, to enable them to exert their ascending forces at the same time.

Line Rockets, or Courantines.

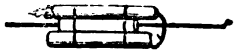
This name is given by the French from *Courant*, or running.

They are about one-half and three-quarter pound rockets of the common kind of sky-rockets. Any number, from 1 to 10, can be used; and, according to the cases, the Courantines are said to be of "so many charges."

When a number are used, a suitable perforated cylinder of light wood is employed, in which the perforations are made, lengthways, exactly through the centre, and as many grooves as there are rockets, are made on its circumference in the same direction, in which they are securely tied with string. The

diameter of the cylinder must be such, that when laid in the grooves, the cases may nearly touch each other. They are so arranged that heads and tails are alternately at the same end of the cylinder, and they are connected by carrying a leader from the tail of one to the head of the other.

FIG. 292.



A small wire is stretched between two posts about 100 yards apart, and the runner placed upon it, when the first rocket is fired, which will carry the whole to the other end, and back, and so on, until the charges are consumed.

These runners are made in the form of dragons, ships, &c., which may be filled with coloured rains, serpents, port-fires, &c.

Revolving Courantines or Pigeon Wheels.

These rockets, while they run along the line, are made to revolve at the same time. This rotatory motion is managed by fixing to the cases another rocket placed in a transverse direction, and in which the aperture is made in the side, near one end. This transverse rocket is filled with a slow charge, in order that it may not burn away too rapidly.

Table Rockets.

This is a simple application of rockets to the spokes of a wheel, to which they form the felloe; they are placed, for exhibition, on a table in the open air. When ignited, they spin round, forming a circle of fire.

A cone of wood is made, to which four spokes can be attached, and on each spoke a 9 inch 1 lb case is fixed. A hole is bored in each case near the clay, and all these holes are made so that the fire of each case may act the same way. Leaders are carried from each hole to the top of the cone, and then all are tied together; the leaders are lighted in the middle, that all the cases may fire at the same time.

Chained Rockets.

The end of some strong thread is tied round the body of one rocket, while a second rocket is fastened to the other end of the thread. Another piece of thread is tied to one of these rockets, and the other end to a third rocket. A leader is then placed in the mouth of each rocket, when they are all hung close together.

The ends of the leaders are tied together and primed. When the priming is fired, the rockets all mount together, separating as far as the strings will permit.

Signal Rockets.

There are two kinds of these rockets, with and without report. The first are made rather longer than usual, and a greater quantity of clay is driven on their charge. The cases and rods of the latter must be made very light, but in other respects they do not differ from ordinary sky-rockets.

They are frequently fired in groups of 6, 8, and 10, and when fixed to one rod, they form a beautiful appearance in their flight, the tail being of great magnitude, and the bursting of so many heads at once, producing a grand explosion.

The Peacock's Tail.

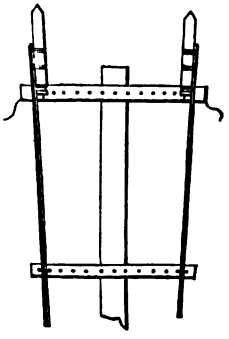
This device consists in placing 20 or more rockets in a frame with the lower ends of the sticks as close to each other as possible, while the others are slightly diverging. When the rockets are fired, they at once fly into the air in the form of the so-called peacock's tail.

The Wing Rocket.

This is similar to all other rockets with respect to case and composition, except that it is discharged from a tube adapted to suit the angular position of the wings (Fig. 293).

FIG. 293.

FIG. 294.



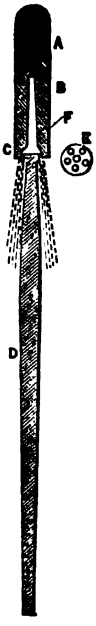
The Girandole.

In this display, the rockets are placed on one or more frames placed behind each other. The sticks rest in small holes on the lower bar of the frame (Fig. 294), and a powerful quick-match is attached to the side of the upper bar, in contact with the quick-matches of the rockets. When fired, the rockets all rise together.

Another arrangement, called *The Girandole chest of Rockets*, consists of a box 6 feet long by 2 feet wide, capable of holding 150 rockets of one-half to three-quarter inch calibre, which is placed on a stand. The sticks pass through holes, about 3 inches apart, in the top of the box. These holes are connected by means of grooves, in which the quick-match is placed. The bottom is also perforated with holes of a smaller diameter. The rockets are then placed in the holes, so that their mouths rest on the quick-match in the grooves, and when any part of the match is ignited, all the rockets are immediately fired.

War Rockets.

FIG. 295.



These rockets were, at first, precisely similar in form to the common sky-rocket, the cases being made of iron, instead of paper. Their present construction is thus explained by Dr. Scoffern in his interesting volume on "Projectile Weapons of War."

The part A (Fig. 295) indicates the piece of iron attached to the end of the rocket, and serving as a shot, or a shell &c. B corresponds with the body of the rocket, filled with composition and perforated as in a common rocket; the base of this conical opening expands into a chamber, F, in order to bursting the rocket. C represents a sectional view of a piece of gun metal, a front view of which is shown by E. The great peculiarity of the congreve rocket consists in this piece, the iron with which the stick is armed being screwed into the central opening, while the five peripheral orifices communicating with the hollow cone (the section of two only are seen in the diagram), serve as vents to the flame, and correspond with the one central opening in the common sky-rocket. When the rocket composition burns out, the shell charge is not immediately ignited, but takes fire by means of a fuse; portions of which can be drilled out through a screw plugged hole in the shell

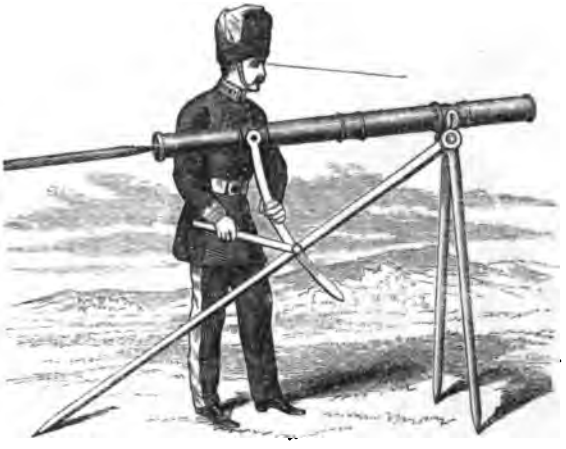
extremity of the rocket, so as to time the explosion of the shell.

The rocket, carried by its own impulse, requires no ordnance to project it, and, therefore, has the advantage of great portability. Another recommendation of the rocket, is its freedom from recoil. Rapidity of discharge and concentration of fire, are also other advantages of the rocket, as it only requires to be placed in the intended direction and fired. Another characteristic of the rocket, is the devastating effect of its fiery train, burning everything in its course, exploding ammunition waggons, mowing down troops, and producing inextricable confusion among cavalry.

The apparatus for directing rockets in their course, is of a tubular nature; but they are also simply laid on the ground, and fired in what is termed *the ground volley*. The rocket tube is shown in Fig. 296, the necessary angle being taken by means of a *hausse*, or tangent scale.

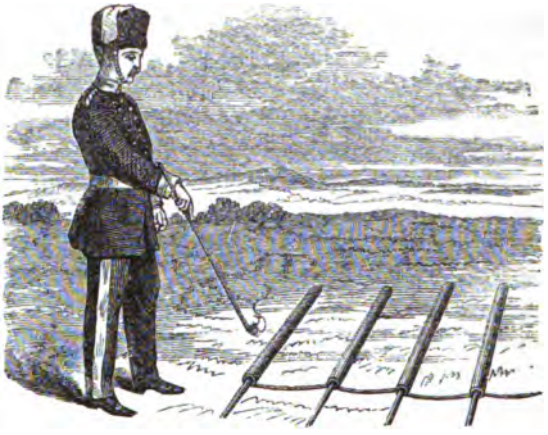
When large numbers of rockets are to be fired at once, the ground volley answers every purpose. This arrangement consists in laying any number of rockets on the ground at fixed distances from each other, connecting them by a quick-match, and then firing them in rapid succession. Fig. 297 represents this arrangement.

FIG. 296.



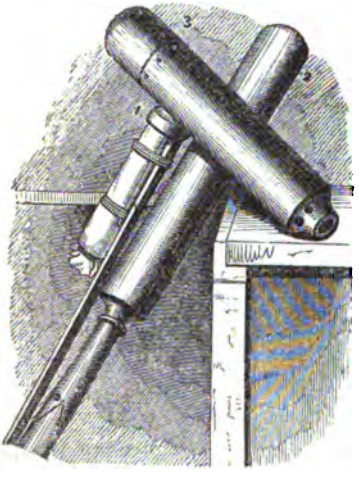
Mr. Hale has contrived to give the rocket flight without the aid of the stick. In Hale's rocket there are two tangential apertures,

FIG. 297.



placed centrally, or rather coincident with the plane of the centre of gravity of the rocket. These rockets are ignited at one of the mesial apertures, whence the fire communicates through the whole perforation of the rocket. A part of the products of combustion passes through these holes, but the greater portion escapes through the central hole where the stick would be, if it had been an ordinary congreve rocket.

FIG. 298.



Hale's newest form of rocket may be likened to a pair of rockets joined together and separated by a diaphragm of iron, perforated by a touchhole. Each rocket of this compound one has its own specific function. The anterior one furnishes gas for the two tangential holes, while the posterior one supplies the flame of propulsion, and the touchhole merely obviates the necessity of igniting the rocket in two places.

The great difficulty attending the use of the war rocket, is to give it a correct flight in starting, for its first movement is weak, the head droops, and thus a departure from the intended course

is apt to ensue. Mr. Hale has endeavoured to overcome this difficulty, by confining his rocket in a sort of cage, until a certain initial force is acquired, when, by the pressure of a spring, the cage opens, and the rocket is left free, as to its whole length; in mid-air obedient to the law of gravity, it then tends to fall, but the drooping of its head is obviated to a great extent.

Another arrangement of Mr. Hale's, relates to the use of rockets on board men-of-war. He employs a large bent tubular pipe like the letter U, with both its heels projecting out of a port-hole. The rocket, having no stick, can find its way round the bend of the pipe. By this device, the back fire of the rocket is actually turned against the enemy.

Rockets without Rods.

This arrangement consists in attaching four triangular pasteboard wings, lengthways on the outside of the cartridge, similar to those used with arrows. The rocket is placed over a hole in a board and fired from below, or the four wings rest on as many iron pins, 6 or 8 inches long, driven into a block of wood, and the rocket is fired from between them.

Scrolls for Rockets.

These scrolls consist of cases, both ends being pinched close, and small holes are made in the reverse sides. They are primed with meal powder, moistened with spirits of wine.

The heads of the rockets are filled with these cases, and when fired, they burst, forming a beautiful spiral descent.

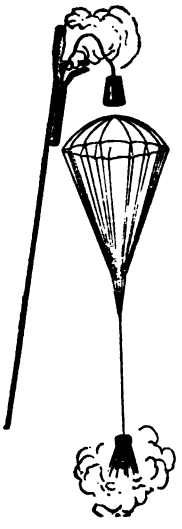
Luminous Rods for Rockets.

This is a device of Chertier, who employs sticks made a little lighter than usual. The rod is coated with strong paste, and then rolled among some coloured composition. After it has become dry, the loose composition is rubbed off with a soft brush, and the above treatment is repeated three or four times in succession. The rod is then rolled in fine gunpowder and a leader is attached lengthways, the end being connected with the rocket.

The Parachute Signal Light,

Or rocket, is the invention of Colonel Boxer, and presents a splendid appearance.

FIG. 299.



It consists of a box open at one end and filled with a flame composition. It is attached to a parachute, by which it is supported in the air. The whole is forced into a sheath and made fast in the pot of a fusee.

The instructions for making the parachute are as follow :—Cut out of the jaconet square pieces of 42 inches the side, according to the required number of parachutes. Place these square pieces in parcels of twelve, and fix one of these parcels on a table by means of four nail pins, without heads, driven in at the four corners; the material being evenly stretched and without any crease. Plant a nail in the centre of the square and trace the circumference of the parachute with a radius of 21 inches; measure out fifteen equidistant points on the circumference; prick them with a packing needle, and cut out the twelve circles. The whipcord must be cut into pieces of 31½ and 22½ inches in length, and a knot made at one of the ends of the pieces, 22½ inches long. Some squares of 11½ inches the side are then cut out of the remnants of the material. Stick at each point, marked in the circumference of the parachutes, one of the strings of 22½ inches long, the end of which has a knot, using glue and the square pieces of material.

Fig. 299 presents the appearance of this signal light.

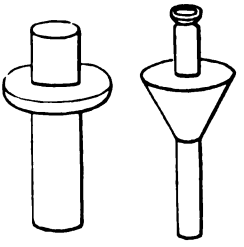
V. AQUATIC FIREWORKS.

These pyrotechnical displays are among the most remarkable and interesting of fireworks.

All the devices which come in contact with the water, ought to be covered with a coating of tallow or grease, and all pipes for communication under the water, must be made of thicker paper, than that used for terrestrial fireworks. These pipes ought to be dried and washed with a drying oil, and all joints after being made, ought to be prepared in a similar manner.

Fire Balls, &c.

FIG. 300.



These pieces are prepared as already described, but they must be weighted underneath with sand, or some similar material, to the extent of half the weight of the case. Fire wheels must also be attached, as shown in Fig. 300.

Fire Globes.

The bowls for these water-globes must be very large, with wheels on them of ten sides. A piece of wood is nailed on each side, with a groove on the outside, wide enough to receive the fourth of a four ounce case, which are connected by leaders in the usual manner. An upright iron spindle is fixed in the centre of the wheel, which serves as an axis for the globe, which must stand 4 or 6 inches above the wheel. All the port-fires must be placed with their mouths outwards and clothed with leaders. The plan for firing the wheel consists in carrying a leader from the mouth of one of the first cases to that of the other, when the leader, having been burnt through the middle, will fire both at the same time.

Floating Suns.

These suns are formed by fastening four cases round a circular wooden dish, so weighted as to sink two-thirds in the water. It is advisable to cover it with paper coated with grease, to prevent the entrance of water from above.

FIG. 301.

When the dish is charged with stars, and a quantity of gunpowder, it explodes at the conclusion, in imitation of the swarming of bees.

Water Mines.

A bowl with an ordinary wheel, with a hole in the middle for the mine, is employed for this device. The mines are tin pots with strong bottoms, fixed in the hole in the wheel, the bottom resting on the bowl. The mines are filled with serpents, crackers, stars, &c., and a case of Chinese fire fixed in the centre or small gerbe, which must be lighted at the beginning of the last case on the wheel.

Water Fire-Fountains.

A wooden float, three feet in diameter, carries a round perpendicular post in the middle, 4 feet high and 2 inches diameter. Three circular wheels, without spokes, are fixed round this post, the largest being nearly of the same diameter, and within three inches of the float. The smallest wheel is 16 inches diameter and placed about 6 inches from the top of the post. Eighteen 4 or 8 oz. cases of brilliant fire are placed round the first wheel, with their mouths outwards. Thirteen and eight similar cases are placed on the middle uppermost wheels, with a gerbe on the top of the post. All the cases and gerbe are connected by leaders, so as to take fire at the same time.

This device produces a very beautiful effect.

Water Rockets.

When the rockets are heavy, they must be kept above the water by means of cork floats. The cases for these rockets are made in the same manner as those for sky-rockets, but with thicker paper. A ladleful of slow fire is first driven in, then two of the proper charge, and afterwards one or two ladles of the sinking charge, and so on, until the case is filled within three diameters. A ladleful of clay is now driven in upon the composition, and a small hole made through the clay to the charge. The case is then securely filled with corn-powder, on which two or three rounds of the case are turned down in the inside. The end is now pinched and tied, when it is dipped in melted resin or sealing-wax.

Six or eight of these rockets are thrown into the water and fired at the same time.

Swans and Ducks.

These and other devices, such as Neptune in his chariot, fire ships, &c., are all made to represent these objects and charged with various fireworks, according to the taste or design of the parties.

THEORETICAL AND GENERAL NOTICES.

The action of the various chemical mixtures, described in the previous pages, depends on the presence of oxygen and some other substances with which it can combine, under the influence of a high temperature.

The substances employed for yielding the oxygen are certain salts of nitric or chloric acid, and among the other materials, the most important are sulphur, carbon, and various metals, and organic compounds.

Among the latter, sulphur and carbon are the most suitable, as they yield gaseous products by their union with the oxygen, leave no residue, and are more easily managed than the organic compounds, such as resin, fats, &c. The few metals employed are for the production of coloured flames.

The most useful compounds of the nitric and chloric acids, viz., the potash-salts, not being hygrometric, present many advantages in mixtures of this description; the chlorate is preferable, as it is decomposed at a lower temperature than the nitrate. The latter requires to be fused before decomposition ensues, while the former is decomposed as it arrives at this point, which is also lower than the melting point of nitrate of potash. This is shown by the following experiment: a piece of silver being placed in a mixture of nitrate of potash, sulphur, and antimony, and heat applied, ignition takes place, and the silver fuses, while it remains unmelted in a similar mixture with the chlorate of potash.

The great object in pyrotechnics being to please the eye with as great a variety as possible, it has been found necessary in practice sometimes to employ the one salt and sometimes the other, in order to take advantage of the difference in the mode of action of these two salts.

With regard to the preparation of the materials, there are two important and well-recognized facts, viz., that the rapidity of the combustion of a pyrotechnic mixture depends upon the degree of fineness of the materials and the density of the mixture, the former increasing and the latter diminishing the speed of the combustion. The explanation of these facts has been given in a previous chapter on the manufacture of gunpowder.

All pyrotechnic mixtures give rise to a combustion, accompanied either with glowing particles or with flame. The former consist of glowing particles which burn in the atmosphere, or only remain in this condition as long as their original temperature is sufficient.

There are only three substances which the pyrotechnist can use for the production of sparks which will burn in the atmosphere, viz., charcoal, zinc, and carbide of iron; and in the preparation

of mixtures for this purpose, it is essential that they shall not contain more oxygen than is necessary to produce sufficient heat to ignite these substances. A larger proportion of oxygen would oxidize these bodies, and the peculiar effect produced by their combustion in the air would be anticipated.

The materials for the production of flame, which are employed in fireworks, consist of sulphur, metals, and hydrogen, and the requisite colour of the flame regulates the choice of the substances as well as the character of the mixture. Thus, for *white colours*, there is always a tinge of blue, yellow, green, or red, varying with the nature of the mixture. The two substances which are most commonly used are sulphide of antimony and sulphide of arsenic. Sulphide of tin produces a very beautiful white-coloured flame, but as this substance is liable to decomposition, it cannot be employed in ordinary circumstances. Osmium is also said to yield a pure white flame.

Blue colour.—There is only one substance which produces a blue-coloured flame, and this only under certain conditions. Antimony, and organic substances are sometimes employed, but the colour of the former is dull and grey, while the latter only yields the faint blue light of carbonic oxide.

When copper is burnt in a hydrogen flame, it communicates a distinct grass-green colour, but the moment a little free chlorine is introduced, the colour acquires a perfectly blue character. It is for this reason that calomel is employed in those mixtures which contain copper, intended to yield a blue colour.

Chloride of ammonium is also employed for a similar object; but the use of this salt along with chlorate of potash is attended with danger.

Acetate of copper, mixed with chlorate of potash and sulphur, gives a fine deep blue colour, but nearly all the mixtures of other salts of copper, furnish flames tinged more or less with green.

Yellow colour.—This colour is one of the most easily managed in pyrotechny, and soda in any form can be employed.

Green colour.—There are only two substances which produce a green colour, viz., copper and barium.

Copper only yields a pure green flame when burnt in hydrogen, and this is even uncertain, as the least difference in the temperature causes the green colour to disappear. The flame of sulphur destroys the green colour obtained from copper; when a mixture of sulphur and oxide of copper is placed in oxygen, a pale yellow

flame is produced, but if any substance containing hydrogen is added, the flame acquires a beautiful green colour. An organic substance must therefore be always one of the constituents of these mixtures. Chlorate of copper produces a magnificent green.

Red colour.—The salts of strontia give such beautiful red colours that it is unnecessary to employ any other material.

The carbonate of lithia produces a fine purple-red colour, but its cost is so great that it cannot be used on ordinary occasions.

STATISTICS OF THE TRADE.

We are indebted to Mr. H. W. Darby, the ingenious pyrotechnist, for the following information as to the annual value of the fireworks consumed in the United Kingdom; and from his intimate knowledge of this manufacture, the statements may be considered as correct.

In ordinary years, the value of the fireworks purchased by and for the public, amounts to from £15,000 to £20,000, which rises to £25,000 in a coronation year.

When national rejoicings celebrate the termination of a war, as in the case of the Russian war, he estimates the amount at £26,000, which was far exceeded on the occasion of the marriage of the Prince of Wales, when the value was upwards of £30,000.

END OF PART IV.

LONDON : *October* 1865.
219 REGENT STREET.

PUBLICATIONS

OF

H. BAILLIÈRE

IN

MEDICAL AND THE COLLATERAL SCIENCES.

TO WHICH IS ADDED

A LIST OF SCIENTIFIC AMERICAN AND FRENCH WORKS.

NEW YORK.
BAILLIÈRE BROTHERS,
440 BROADWAY.

PARIS.
J. B. BAILLIÈRE ET FILS,
RUE HAUTEFEUILLE.

MELBOURNE (AUSTRALIA).
F. F. BAILLIÈRE,
COLLINS STREET EAST.

MADRID.
BAILLY BAILLIÈRE,
CALLE DEL PRINCIPE.

Anatomy.—Muscular Anatomy of the Horse. By James I. Lupton, M.R.C.V.S. 8vo. with 12 Woodcuts. 1862. 3s. 6d.

Anatomy of the External Form of the Horse, with Explanations. By James I. Lupton, M.R.C.V.S. Part I., with 9 Plates, large folio. Price, plain, £1 11s. 6d.; India paper, £2 5s. Part II., with 4 Plates, price, plain, 15s.; India paper, 20s. *The Plates of the Mouth and Leg are coloured.*

*** This Work will be completed in Three Parts, consisting of 18 to 20 Plates, with Explanations, and a volume 8vo. of Text, giving the Study of the External Form of the Horse and the Physiology of Locomotion.

Ashley (W. H.)—A Practical Treatise on Vesicular Hydatids of the Uterus. 1856. 2s. 6d.

Atkinson.—Physics. (*See* Ganot.)

Austin (Thos.)—The Millstone Grift, its Fossils in the Bristol District. 8vo. with 4 Plates. London, 1865. 4s.

Baudens.—On Military and Camp Hospitals, and the Health of Troops in the Field. Translated by F. B. Hough, M.D. 12mo. New York, 1862. 6s.

Berkeley (Rev. J. M.)—Introduction to Cryptogamic Botany. 8vo. illustrated with 127 Engravings. London, 1857. £1.

Bernard and Huette.—Illustrated Manual of Operative Surgery and Surgical Anatomy. Edited, with Notes and Additions, by W. H. Van Buren, M.D., Professor of Anatomy, University Medical College, and C. E. Isaacs, M.D. Complete in 1 vol. 8vo. with 118 coloured Plates, half-bound morocco, gilt tops. New York, 1864. £3 4s.

Birch.—On the Therapeutic Action of Oxygen; with Cases proving its singular Efficacy in various Intractable Diseases. 8vo. 1857. 2s. 6d.

Boenninghausen.—Manual of Homœopathic Therapeutics, Guide to the Study of Materia Medica Pura. Translated, with Additions, by J. Laurie, M.D. 8vo. 1848. 12s.

Boenninghausen.—Essay on the Homœopathic Treatment of Intermittent Fevers. 8vo. New York, 1845. 2s. 6d.

Boussingault.—Rural Economy; in its Relation with Chemistry, Physics, and Meteorology. By J. B. Boussingault, Member of the Institute of France. 2nd Edition. 8vo. boards. London, 1845. 18s.

ampbell.—A Practical Text-Book of Inorganic Chemistry, including the Preparation of Substances, and their Qualitative and Quantitative Analyses, with Organic Analyses. By D. Campbell, Demonstrator of Practical Chemistry to the University College. 12mo. 5s. 6d.

anton (A.)—The Teeth and their Preservation, in Infancy and Manhood to Old Age. 12mo. with Woodcuts. 4s.

hapman.—A Brief Description of the Characters of Minerals. By Edward J. Chapman, Professor in the University of Toronto (Canada). 12mo. with 8 Plates. London, 1844. 4s.

hapman.—Practical Mineralogy; or, a Compendium of the distinguishing Characters of Minerals; by which the Name of any Species may be speedily ascertained. 8vo. with 13 Engravings, showing 270 specimens. London, 1843. 7s.

hemical Society (Quarterly Journal of the). 14 vols. 8vo. London, 1848-61. Vols. I. to IX. have been reduced to 6s. each; vols. X. to XIV., 18s. each. Or in Quarterly Parts, price 8s. each.

*** This Journal, beginning with Vol. XV., is now issued Monthly. Price (the Year), 12s.

ruveilhier and Bonamy.—Atlas of the Descriptive Anatomy of the Human Body. By J. Cruveilhier. With Explanations by C. Bonamy. Containing 82 Plates of Osteology, Syndemology, and Myology. 4to. London, 1844. Plain, £3. Coloured Plates, £5 15s.

Vol. II. On the Circulation of the Blood, French Text, 4to. coloured Plates, £3 4s.

Vol. III. On the Digestive Organs and Viscera, French Text, coloured Plates, £3 6s.

urie (P. F., M.D.)—Principles of Homœopathy. 1 vol. 8vo. London, 1837. 5s.

ay (G.)—Chemistry in its Relation to Physiology and Medicine. 8vo. with 5 coloured Plates. London, 1860. £1. Reduced to 10s.

eleuze.—Practical Instruction in Animal Magnetism. 4th Edition, 1850. 4s. 6d.

ick (H.)—Gleet: its Pathology and Treatment. By H. Dick, M.D. 8vo. London, 1858. 8s. 6d.

rysdale (C. R.)—On the Treatment of Syphilis and other Diseases without Mercury. 8vo. London, 1863. 2s. 6d.

Drysdale (C. R.)—Remarks on the Antecedents and Treatment of Consumption. 8vo. 1s.

Dumas and Boussingault.—The Chemical and Physiological Balance of Organic Nature: an Essay. 1 vol. 12mo. London, 1844. 4s.

Edwards (A. M.)—Life beneath the Waters; or, the Aquarium in America. 12mo. beautifully illustrated. New York, 1858. 7s. 6d.

Ethnographical Library. Vol. I. The Native Races of the Indian Archipelago. Papuans. By G. W. Earl. Post 8vo. Illustrated with 5 coloured Plates, 2 Maps, and Woodcuts. London, 1853. 10s. 6d. Reduced to 5s.

Ditto. Vol. II. The Russian Races. By R. Latham, M.D. With a Map and coloured Plates. 1854. 8s. Reduced to 5s.

Fau.—The Anatomy of the External Forms of Man, for Artists, Painters, and Sculptors. Edited by R. Knox, M.D. 8vo. Text, and 28 4to. Plates. London, 1849. Plain, £1 4s. Coloured £2 2s.

Fielding and Gardner.—Sertum Plantarum; or Drawings and Descriptions of Rare and Undescribed Plants from the Author's Herbarium. 8vo. London, 1843. £1 1s. Reduced to 10s. 6d.

Flourens (P.)—On Human Longevity, and the Amount of Life upon the Globe. Edited by C. Martel. 12mo. London, 1855. 3s.

Gamgee (J. S.)—Researches in Pathological Anatomy and Clinical Surgery. With 6 Plates. London, 1856. 9s.

Ganot.—Elementary Treatise on Physics, Experimental and Applied. Translated on the 9th Original Edition by Dr. Atkinson, of the Royal Military College, Sandhurst. With 600 Illustrations. Post 8vo. 1862. 12s. 6d.
(*Adapted for the use of Colleges and Schools.*)

Gerber and Gulliver.—Elements of the General and Microscopical Anatomy of Man and the Mammalia; chiefly after Original Researches. To which is added an Appendix, comprising Researches on the Anatomy of the Blood, Chyle, Lymph, Thymous Fluid, Tubercle, by C. Gulliver, F.R.S. 8vo. and an Atlas of 34 Plates. 2 vols. 8vo. 1842. £1 4s. Reduced to 15s.

Gesner (A.)—A Practical Treatise on Coal, Petroleum, and other Distilled Oils. 2nd Edition, enlarged. Illustrated with 42 Figures, and a View on Oil Creek, in Pennsylvania. 8vo. New York, 1865. 10s. 6d.

Gill (J. B.)—An Epitome of Surgery. 18mo. London, 1860. 1s.

Gordon (S.)—A Synopsis of Lectures on Civil Engineering and Mechanics. 4to. London, 1849. 7s. 6d.

Grant.—General View of the Distribution of Extinct Animals. In the 'British Annual,' 1839. 18mo. London, 1839. 3s. 6d.

Grant.—Outlines of Comparative Anatomy. 8vo. 148 Woodcuts. London. £1 8s. Reduced to **£1.**

Grant.—On the Principles of Classification, as applied to the Primary Divisions of the Animal Kingdom. In the 'British Annual,' 1838. 18mo. illustrated with 28 Woodcuts. London, 1838. 3s. 6d.

Graham.—Elements of Chemistry; including the application of the Science in the Arts. By T. Graham, F.R.S. L. & E., Master of the Mint. 2nd Edition, revised and enlarged, illustrated with Woodcuts, 2 vols. 8vo. £2.
Ditto. Vol. II. Edited by H. Watts, M.C.S. Separately. 1857. £1.

Greatest (The) of our Social Evils: Prostitution as it now exists in London, Liverpool, Manchester, Glasgow, Edinburgh, and Dublin; an Inquiry into the Cause and Means of Reformation, based on Statistical Documents. By a Physician. 12mo. London, 1857. 5s. Reduced to **3s. 6d.**

Hahnemann.—Lesser Writings. Collected and Translated by R. E. Dudgeon. 8vo. London, 1857. £1 1s.

Hall (Marshall).—On the Diseases and Derangements of the Nervous System, in their Primary Forms, and in their Modifications by Age, Sex, Constitution, Hereditary Predisposition, Excesses, General Disorder, and Organic Disease. 8vo. with 8 Engraved Plates. London, 1841. 15s.

Hall.—On the Mutual Relations between Anatomy, Physiology, Pathology, Therapeutics, and the Practice of Medicine: being the Gulstonian Lectures for 1842. 8vo. with 2 coloured Plates and 1 plain. London, 1842. 5s.

Hall.—New Memoir of the Nervous System, True Spinal Marrow, and its Anatomy, Physiology, Pathology, and Therapeutics. 4to. with 5 Plates. London. £1.

Hamilton.—A Guide to the Practice of Homœopathy. Translated and Compiled in Alphabetical Order from the German of Ruoff, Haas, and Ruckert, with Additions. 12mo. 1844. 5s.

Hamilton.—Flora Homœopathica; or Illustrations and Descriptions of the Plants used as Homœopathic Remedies. 2 vols. 8vo. with 66 coloured Plates. 1851. £3 10s.

Hamilton.—Practical Treatise on Military Surgery and Hygiene. 8vo. with 127 Engravings. New York, 1865. £1.

Hooker.—Icones Plantarum. By Sir W. J. Hooker. New Series. Vols. I.—IV., containing 100 Plates each, with Explanations. 8vo. cloth. London, 1842–1844. Each vol. £1 8s. Reduced to **10s.**

Hooker.—The London Journal of Botany. Vols. I.—VI., with 24 Plates each, boards, 1842–1847. Now reduced to **£4.**

Hooker.—Niger Flora; or, an Enumeration of the Plants of Western Tropical Africa. Collected by the late Dr. T. Vogel, Botanist to the Voyage of the Expedition sent by Her Britannic Majesty to the River Niger in 1841, including Spicilegia Gorgonea, by P. B. Webb, and Flora Nigritiana, by Dr. J. D. Hooker and George Bentham. With 2 Views, a Map, and 60 Plates. 8vo. London, 1849. £1 1s. Reduced to **10s. 6d.**

Hooker.—Notes on the Botany of the Antarctic Voyage conducted by Captain James Clark Ross, R.N., in H.M.S. *Erebus* and *Terror*; with Observations on the Tussac Grass of the Falkland Islands. 8vo. With 2 Plates. London, 1843. 4s.

Horse (*See* Anatomy of the).

Hufeland.—Manual of the Practice of Medicine; the Result of Fifty Years' Experience. Translated by C. Bruchhausen and R. Nelson. 2nd Edition. 8vo. London, 1858. 7s. 6d.

Hulme (E. T.)—Contributions to Dental Pathology. Calcification of the Dental Pulp. Three Lectures on the Diseases of the Dental Periosteum. 3 Plates. 8vo. London, 1862. 2s. 6d.

Humboldt.—Kosmos: a General Survey of the Physical Phenomena of the Universe. The original English Edition. 2 vols. post 8vo. Reduced to **10s. 6d.**

Isherwood (B. E.)—Engineering Precedents for Steam Machinery: embracing the Performances of Steamships, Experiments with Propelling Instruments, Condensers, Boilers, &c., accompanied by Analyses of the same; the whole being original matter, and arranged in the most practical and useful manner for Engineers. 2 vols. 8vo. With Plates and Tables. New York. 15s.

Kæmtz.—A Complete Course of Meteorology. With Notes by Ch. Martins, and an Appendix by L. Lalanne. Translated, with Additions, by C. V. Walker. Post 8vo. With 15 Plates. 12s. 6d.

Knox (R.)—Man; his Structure and Physiology, popularly explained and demonstrated, by the aid of 8 movable dissected coloured Plates and 5 Woodcuts. 2nd Edition, revised. Post 8vo. London, 1858. 10s. 6d.

*** This work is written especially for the use of Students who intend graduating in Arts at the English Universities.

Latham (R. G.)—The Native Races of the Russian Empire. 12mo. With a Map and coloured Plates. London, 1854. 5s.

Lebaudy.—The Anatomy of the Regions interested in the Surgical Operations performed upon the Human Body; with Occasional Views of the Pathological Condition which render the interference of the Surgeon necessary. 24 Plates. Folio. London, 1845. £1 4s.

Lee.—The Anatomy of the Nerves of the Uterus. Folio, with 2 Plates. London, 1845. 8s.

Liebig.—Chemistry and Physics, in relation to Physiology and Pathology. 2nd Edition, 8vo. London, 1847. 3s.

Lobb.—Curative Treatment of Paralysis and Neuralgia with the aid of Galvanism. 12mo. 2nd Edition. 1859. 5s.

Lupton.—(*See* Anatomy of the Horse.)

Massy.—Analytical Ethnology; the Mixed Tribes in Great Britain and Ireland Examined, and the Political, Physical, and Metaphysical Blunderings on the Celt and the Saxon exposed. 12mo. Plates. 5s.

Memoirs of the Literary and Philosophical Society of Manchester. 3rd Series. Vol. I. 8vo. or Vol. XX. of the Collection. With Woodcuts and Plates. London, 1862. £1.

Miers (J.)—Illustrations of South American Plants. 2 vols. 4to. 84 Plates. £3 14s.

Ditto. Vol. II. 42 Plates. 1857. £1 17s.

Mitchell (J.)—Manual of Practical Assaying, intended for the use of Metallurgists, Captains of Mines, and Assayers in General. With copious Tables, for the purpose of ascertaining in Assays of Gold and Silver the precise amount, in Ounces, Pennyweights, and Grains, of noble metal contained in one ton of Ore from a given quantity. 2nd Edition, 8vo. much enlarged, with 360 Illustrations. London, 1854. £1 1s.

Mitchell (J.)—Treatise on the Adulterations of Food, and the Chemical Means employed to detect them. Containing Water, Flour, Bread, Milk, Cream, Beer, Cider, Wines, Spirituous Liquors, Coffee, Tea, Chocolate, Sugar, Honey, Lozenges, Cheese, Vinegar, Pickles, Anchovy Sauce and Paste, Catsup, Olive Oil, Pepper, Mustard. 12mo. 1848. 6s. Reduced to **3s.**

Moquin-Tandon.—Elements of Medical Zoology; a Description of the Animals used in Medicine, as well as of those Species which are Injurious to or are Parasitic upon Man. Edited by R. T. Hulme. With 124 Illustrations. 1861. 12s. 6d.

Moreau (Professor).—Icones Obstetricæ; a Series of 60 Plates and Text, illustrative of the Art and Science of Midwifery in all its Branches. By M. Moreau, Professor of Midwifery to the Faculty of Medicine, Paris. Edited by J. S. Streeter, M.R.C.S. Folio. 1841. Plain, £3 3s.

Morel (C.)—Compendium of Human Histology. Edited by W. H. Van Buren, M.D. 8vo. with 28 Plates. New York, 1861. 14s.

Mueller (F.)—Fragmenta Phytographiæ Australiæ. 3 vols. 8vo. with Plates. Melbourne, 1860–64. £2 14s.

Mueller (F.)—The Plants Indigenous to the Colony of Victoria. Vol. I. 4to. *Thalamiflorœ.* With 23 Plates. Melbourne, 1860–62. £3 3s.

Muller.—Principles of Physics and Meteorology. By J. Muller, M.D. Illustrated with 530 Woodcuts and 2 coloured Plates. 8vo. London, 1847. 18s.

Newman (George).—Homœopathic Family Assistant. 3rd Edition. 18mo. 1859. 3s. 6d.

Nichol.—The Architecture of the Heavens. By J. P. Nichol, Professor of Astronomy in the University of Glasgow. 9th Edition, entirely revised and greatly enlarged. Illustrated with 23 Steel Engravings and numerous Woodcuts. 8vo. London, 1851. 16s.

Noeggerath and Jacobi.—Contributions to Midwifery, and Diseases of Women and Children; with a Report on the Progress of Obstetrics, and Uterine and Infantile Pathology. 8vo. New York, 1858. 15s.

Norris (E.)—(*See* Ethnographical Library, and Prichard.)

Otto (J.)—Manual of the Detection of Poisons by Medico-Chemical Analysis. By J. Otto, Professor of Chemistry in Brunswick, Germany. With Illustrations. 12mo. New York, 1857. 6s.

Owen (R.)—Odontography; or, a Treatise on the Comparative Anatomy of the Teeth, their Physiological Relations, Mode of Development, and Microscopical Structure in the Vertebrate Animals. This splendid work is now completed. 2 vols. royal 8vo. containing 168 Plates, half-bound russia. London, 1840–45.

Phillips (B.)—Scrofula; its Nature, Prevalence, Causes, and the Principles of Treatment. 8vo. with an Engraved Plate. London, 1846. 12s. Reduced to **5s.**

Pietra Santa.—The Climate of Algiers in reference to the Chronic affections of the Chest. Being a Report of a Medical Mission to Algeria. London, 1862. 1s. 6d.

Prescriber's (The) Complete Handbook. (*See* Trousseau.)

Prichard.—Six Ethnographical Maps. Supplement to the Natural History of Man, and to the Researches into the Physical History of Mankind. Folio, coloured, and 1 sheet of letterpress. 2nd Edition. London, 1860. £1 4s.

Prichard.—On the Different Forms of Insanity, in relation to Jurisprudence. 12mo. London, 1842. 5s.

Prichard (J. C.)—The Natural History of Man; comprising Inquiries into the Modifying Influences of Physical and Moral Agencies on the different Tribes of the Human Family. 4th Edition, revised and enlarged, by Edwin Norris, of the Royal Asiatic Society. With 62 Plates, coloured, engraved on Steel, and 100 Engravings on Wood. 2 vols. royal 8vo. 1855. £1 18s.

Quekett (J.)—Practical Treatise on the use of the Microscope. Illustrated with 11 Steel Plates and 300 Wood Engravings. 3rd Edition, 8vo. £1 1s. Reduced to **12s 6d.**

Quekett (J.)—Lectures on Histology, delivered at the Royal College of Surgeons of England—Elementary Tissues of Plants and Animals. On the Structure of the Skeletons of Plants and Invertebrate Animals. 2 vols. 8vo. Illustrated by 340 Woodcuts. London, 1852–54. £1 8s. 6d. Reduced to **15s.**

Rayer (P.)—A Theoretical and Practical Treatise on the Diseases of the Skin. Translated by R. Willis, M.D. 2nd Edition, remodelled and much enlarged, in 1 thick vol. 8vo. with Atlas, royal 4to. of 26 coloured Plates, exhibiting 400 varieties of Cutaneous Affections. £4 8s.

Richardson and Henry Watts.—Chemistry in its Application to the Arts and Manufactures. 8vo. *Fuel and its Applications.*

Vol. I. Parts 1 and 2, contain Fuel and its Applications. Profusely Illustrated with 433 small Engravings and 4 Plates. £1 16s.

Vol. I. Part 3, contains Acids, Alkalies, Salts, Soap, Soda, Railway Grease, &c., their Manufacture and Applications. With numerous Illustrations. 1864. £1 13s.

Vol. I. Part 4, contains Phosphorus, Mineral Waters, Gunpowder, Gun Cotton, Fire Works, Aluminium, Lucifer Matches. With Illustrations. 1865. £1 1s.

Vol. II. contains Glass, Alum, Potteries, Cements, Gypsum, &c. With numerous Illustrations. £1 1s.

Vol. III. contains Food generally, Bread, Cheese, Tea, Coffee, Tobacco, Milk, Sugar. With numerous Illustrations and Coloured Plates. £1 2s.

*** The Authors of this Edition in their Preface say: 'So rapid has been the growth and so great the development of the branches of Manufacture more intimately connected with Fuel, that, in preparing a Second Edition, we have found it necessary, not only to re-write much of the original, but to extend so considerably the limits of the first group as to occupy the entire of this volume, which may, therefore, with far greater propriety be called a New Work than a Second Edition.'

Reichenbach.—Physico-Physiological Researches on the Dynamics of Magnetism, Electricity, Heat, Light, Crystallization, and Chemism, in their Relations to Vital Force. 2nd Edition, with Additions, Preface, and Critical Notes, by John Ashburner, M.D. 8vo. with Woodcuts, and 1 Plate. London, 1850. 15s.

Reid.—Rudiments of Chemistry, with Illustrations of the Chemistry of Daily Life. 4th Edition, with 180 Woodcuts. 12mo. 1850. 2s. 6d.

Regnault.—An Elementary Treatise on Crystallography, illustrated with 108 Wood Engravings. 8vo. 1848. 8s.

Richardson.—Geology for Beginners; comprising a Familiar Exposition of the Elements of Geology and its Associate Sciences, Mineralogy, Fossil Conchology, Fossil Botany, and Palæontology. 2nd Edition, 8vo. with 251 Woodcuts. 10s. 6d.

Richardson (B.)—Medical History and Treatment of Diseases of the Teeth, and the adjacent structures. 8vo. 8s.

Say (Thos.)—The Complete Writings of, on the Conchology of the United States. 8vo. with 75 Plates, half-bound. New York. Coloured, £2 10s.; Plain, £1 5s.

Say (Thos.)—The Complete Writings of, on the Entomology of North America. Edited by J. Le Conte, with a Memoir by G. Ord. 8vo. with 54 coloured Plates. 2 vols. New York, 1859. £4.

Schleiden.—The Plant, a Biography, in a Series of Fourteen Popular Lectures on Botany. Edited by A. Henfrey. 2nd Edition, 8vo. with 7 coloured Plates and 16 Woodcuts. London, 1853. 15s.

Shuckard.—Elements of British Entomology. Part 1. 1839. 8vo. with Figures. 8s.

Shuckard.—Essay on the Indigenous Fossorial Hymenoptera; comprising a Description of the British Species of Burrowing Sand Wasps contained in all the Metropolitan Collections; with their Habits as far as observed. 8vo. with 4 Plates. (Plate I. is wanting.) 10s.

Simpson (M. D.) — Practical View of Homœopathy. 8vo. London. 1836. 10s. 6d.

Smith (S. E.)—Diagnostics of Aural Disease. 8vo. Illustrated with a Plate and 22 Woodcuts. London, 1861. 3s. 6d.

Smith (Stephen)—Handbook of Surgical Operations. 12mo. with 257 Woodcuts. New York, 1865. 8s.

Stars and the Earth.—The Stars and the Earth; or, Thoughts upon Space, Time, and Eternity. 10th Thousand. 18mo. London, 1862. Cloth, 1s. 4d., or paper cover, 1s.

Stevens (W.)—Observations on the Nature and Treatment of the Asiatic Cholera. 8vo. London, 1853. 10s.

Stockhardt.—Chemical Field Lectures for Agriculturists. Translated from the German, with Notes. 12mo. 1853. 4s.

Teste. — A Practical Manual of Animal Magnetism: containing an Exposition of the Methods employed in producing the Magnetic Phenomena, with its Application to the Treatment and Cure of Diseases. Translated by C. Spillan. 18mo. 6s.

Thomson.—Chemistry of Organic Bodies —Vegetables. By Thomas Thomson, M.D., F.R.S. L. & E. 8vo. pp. 1,092. 1838. £1 4s. Reduced to **12s.**

Thomson. — Heat and Electricity. 2nd Edition. 8vo. Illustrated. 15s. Reduced to **7s. 6d.**

Thomson (R. D.)—British Annual and Epitome of the Progress of Science. 3 vols. 1837–38–39. 18mo. each 3s. 6d.

Townshend.—Facts in Mesmerism; with Reasons for a Dispassionate Inquiry into it. 8vo. 9s.

Trousseau and Reveil.—The Prescriber's Complete Handbook to the Principles of the Art of Prescribing, with a List of Diseases and their Remedies, a Materia Medica of the Medicines employed, classified according to their Natural Families, with their Properties, Preparations, and Uses, and a Sketch of Toxicology. Edited by J. B. Nevins, M.D. 1858. 2nd Edition. Roan, limp, 6s. 6d.

Turnbull (L.) — Electro-Magnetic Telegraph; with an Historical Account. 2nd Edition. 8vo. with Plates. 1853. 12s.

Unity of Medicine—(The), its Corruptions and Divisions as by LAW Established in England and Wales: with their Causes, Effects, and Remedies. By a Fellow of the Royal College of Surgeons. 8vo. with a coloured Chart. London, 1858. 7s.

Vogel and Day.—The Pathological Anatomy of the Human Body. Translated, with Additions, by G. E. Day. Illustrated with 100 plain and coloured Engravings. 8vo. 1847. 18s. Reduced to **10s.**

Waterhouse.—A Natural History of the Mammalia: Marsupiata or Pouched, and of the Rodentia or Gnawing Animals. 2 vols. 8vo. Coloured Plates, £3 9s.
Plain, £2 18s.

Weisbach (J.)—Principles of the Mechanics of Machinery and Engineering. 2 vols. 8vo. illustrated with 1,000 Wood Engravings. London, 1848. £1 19s.

Williams (R.)—Elements of Medicine: Morbid Poisons. 2 vols. 8vo. 1836–41. £1 8s. 6d. Reduced to **15s.**
Vol. II. 1841. 18s. Reduced to **8s.**

Willis.—Illustrations of Cutaneous Diseases. A Series of Delineations of Affections of the Skin in their more frequent form. 94 col. Plates. Folio. 1841. £8 8s.

Wilmott.—Glycerin and Cod Liver Oil; their History, Introduction, and Therapeutic Value. 12mo. London, 1859. 3s. 6d.

Wilson (Dr., of Malvern.)—How to Regain Health and Keep it. Popular Lectures on the Preservation of Health and Cure of Chronic Disease. No. 1, 8vo. with Engravings. 1859. 1s. 6d.

Yeldam (S.)—Homœopathy in Acute Diseases. 8vo. 2nd Edition. 1850. 6s. 6d.

AMERICAN

SCIENTIFIC PUBLICATIONS.

Mr. C. E. BAILLIÈRE offers his services to the Profession and the Public for the filling of orders for American Books.

Having just returned after a residence of fifteen years in New York, during which time he was engaged exclusively in the Scientific Book business, he is enabled to give full information relative to American publications; and having his own establishment (not an agency) in New York, he can promise a prompt and faithful execution of all orders entrusted to him.

Gentlemen about to Publish in any of the departments of Science, and wishing to find an American outlet, are requested to communicate with him.

REDUCTION IN THE PRICE OF AMERICAN BOOKS.

Mr. BAILLIÈRE will be happy to execute orders for American Books at the rate of **4s. 2d.** to the **Dollar** nett Cash.

Adams. — Contributions to Conchology. Vol. I. (all published). 8vo. 12s.

Agassiz, L.—Contributions to the Natural History of the United States. Vols. I. to IV. 4to. Boston. Each £2 2s.

American (The) Journal of Insanity. Edited by the Officers of the New York State Lunatic Asylum, Utica. 12 vols. 8vo. cloth, boards. Utica, 1844–56. £7 4s.

American Historical and Literary Curiosities. Consisting of Fac-similes of Documents relating to the Revolution, &c. First and Second Series. 4to. New York. Each £1 12s.

American Association for the Advancement of Science—Proceedings of the. Vols. 1 to 13. Philadelphia, 1849 to 1859. £6 10s.

American Journal of Dental Science. New Series. Vols. II.–IX. Neat half calf. 8vo. Very scarce. Philadelphia, 1851–59. £9.

American Journal of Conchology. Published in Quarterly Numbers of about 100 pages each. With Notes. Conducted by G. W. Tryon. New York, 1865.

American Medical Times (The). Edited by S. Smith. 1860 to 1864. 8 vols. 4to. in cloth, boards. New York. £2 2s.

Australia.—A Complete Description of the whole of the Colony of Victoria. With new Map. The most recent and accurate information as to every Township, Village, and Hamlet; every River, Creek, Mountain, Lake, Goldfield, Road, and Railway in Victoria; with its Botanical, Geological, and Physical features; the division of the Colony into Counties, Ridings, and Electoral, Police, Squatting, Mining, and Municipal Districts; the Names, Areas, Occupiers' Position nearest Post Town, and grazing capabilities of all the Squatting Stations, and the best means of reaching them. 8vo. pp. 442, cloth. £1 1s.

Baird.—Mammals of North America, Descriptions of Species, based chiefly on collections of the Museum of Smithsonian Institution. 4to. 764 pages, and 87 Plates. Philadelphia, 1859. £4 4s.

Barton.—The Cause and Prevention of Yellow Fever at New Orleans and other Cities in America. 3rd Edition. 8vo. with Maps. New York, 1857. 7s. 6d.

Baudens.—On Military and Camp Hospitals, and the Health of Troops in the Field. Translated by F. B. HOUGH, M.D. 12mo. New York, 1862. 5s.

Beck, T. R.—Elements of Medical Jurisprudence. 12th Edition. By C. R. Gilman. 2 vols. 8vo. Philadelphia. £2 10s.

Bedford.—Principles and Practice of Obstetrics. 3rd Edition. 8vo. 1861. £1.

Bedford.—The Diseases of Women and Children. 7th Edition. New York. 16s.

Bell (A. M.)—A Knowledge of Living Things, with the Laws of their Existence. 12mo. with 2 coloured Plates and 60 Woodcuts. New York, 1860. 5s.

Bernard and Huette.—Illustrated Manual of Operative Surgery. With 118 coloured Plates, royal 8vo. half-bound. 1861. £3.

Blake (W. S.)—Observations on the Physical Geography and Geology of the Coast of California, from Bodega Bay to San Diego. 1 vol. 4to. coloured Plates. New York. £2.

Bland and Cooper. — Papers on North American Helicide and on the Geographical Distribution of West India Land Shells. Also Notice of Land and Freshwater Shells from the Rocky Mountains. 8vo. with Plates. New York, 1862. 10s.

Blowpipe.—A System of Instruction in the Practical Use of the: being a Gradual Course of Analyses for the use of Students. 12mo. New York, 1852. 6s.

Brown-Sequard.—Lectures on the Physiology and Pathology of the Central Nervous System, delivered at the Royal College of Surgeons of England, in May 1858. 8vo. with 8 Plates. Philadelphia, 1860. 14s.

Bumstead.—Pathology and Treatment of Venereal Diseases. 8vo. with Illustrations. Philadelphia, 1861. £1.

Canada, Geological Survey of; Figures and Descriptions of Canadian Organic Remains. Sir W. E. LOGAN, Director. Parts 1-4, with Plates. Montreal, 1858-64. £1 5s.

Canada, Geological Survey of, Report of Progress from its Commencement to 1863. Illustrated by 498 Woodcuts. An Atlas of Maps and Sections will shortly be published. 4to. Montreal, 1863. £1 4s.

Canada, Geological Survey of, for the Years 1853-54-55-56. 8vo. And Atlas of Plates and Maps. 4to. £1 10s.

Canada and the Western States of America. Illustrated with 50 Engravings, forming a complete Emigrant's Handbook. 4s.

Canadian (The) Naturalist and Geologist. 8vo. with Illustrations. Vol. 1 to 8. Montreal, 1857-1862. £3 15s. 2nd Series. Vol. 1 to 3. £2 5s.

California, Geological Survey of. Palæontology. Vol. 1, with 32 Plates. 4to. By J. D WHITNEY, State Geologist. 1864. £1 7s. 6d.

Cooper and Suckley.—The Natural History of Washington Territory; with much relating to Minnesota, Nebrasca, Kansas, Oregon, and California. 55 Plates of Botany and Zoology, and Isothermal Chart. 4to. New York, 1859. £2 2s.

Da Costa.—Medical Diagnosis; with special reference to Practical Medicine. Illustrated. 8vo. Philadelphia. £1 1s.

Dalton's Treatise on Human Physiology. 2nd Edition. New York, 1861. £1 1s.

Dana.—A Manual of Geology. 8vo. Philadelphia. 16s. 6d.

Dawson.—Air-Breathers of the Coal Period: a Descriptive Account of the Remains of Land Animals found in the Coal Formations of Nova Scotia. 8vo. with 6 Plates. Montreal, 1863. 6s.

Draper.—Human Physiology, Statical and Dynamical, &c. 8vo. 1856. £1 1s.

Durkee (S.)—A Treatise on Gonorrhœa and Syphilis. 2nd Edition. 8vo. with 8 coloured Plates. Philadelphia, 1864. £1 1s.

Dunglison.—Dictionary of Medical Science. 2nd Edition. 8vo. Philadelphia, 1865. £1 5s.

Emory.—Report of the United States Mexican Boundary. 2 vols. 4to. with 349 coloured and plain Geological Plates. New York, 1858. £5 5s.

Gesner.—A Practical Treatise on Coal, Petroleum, and other Distilled Oils. 2nd Edition. 8vo. with 40 Woodcuts. New York, 1865. 10s. 6d.

Gibbes (L. R.)—Rules for the Accentuation of Names in Natural History; with Examples, Zoological and Botanical. 4to. Charleston, 1860. 2s.

Grace (W.)—The Army Surgeon's Manual, for the Use of Medical Officers, Cadets, Chaplains, and Hospital Stewards. 12mo. New York, 1864. 6s.

Gray (Asa). — Chloris Boreali-Americana. Illustrations of New and Rare North American Plants. 4to. 7s. 6d.

Gross.—Practical Treatise on the Urinary Organs. 8vo. 1851. £1 1s.

Gross.—Elements of Pathological Anatomy. 8vo. Illustrated. New Edition. 1857. £1 1s.

Gross.—System of Surgery; Pathological, Diagnostic, Therapeutic, and Operative. With 936 Illustrations. 2nd Edition. 2 vols. 8vo. Philadelphia. 1862. £2 16s.

Hall (J.) and Whitney.—Report on the Geological Survey of the State of Iowa. Vol. I. 4to. In two Parts, illustrated with 27 steel Engravings, and numerous Woodcuts. Iowa, 1858. £2 10s.

Hall and Whitney.—Report on the Geological Survey of the State of Wisconsin. Vol. I. 4to. 1862. £1 10s.

Hamilton.—Practical Treatise on Fractures and Dislocations. 8vo. with 289 Woodcuts. Philadelphia, 1860. £1 1s.

Harris.—The Principles and Practice of Dental Surgery. 5th Edition, 8vo. with 200 Woodcuts. £1 5s.

Hitchcock.—Ichnology of New England; a Report on the Sandstone of the Connecticut Valley, especially its Fossil Footmarks. 4to. with 60 Plates. £1 15s.

Hitchcock.—An Attempt to Discriminate and Describe the Animals that made the Fossil Footmarks of the United States, and especially of New England. 4to. 15s.

Hitchcock and Hager.—Report on the Geology of Vermont. 2 vols. 4to. 1861. £2 5s.

Hodge.—On Diseases Peculiar to Women. 8vo. with Illustrations. Philadelphia. 14s.

Hodge (H. L.)—The Principles and Practice of Obstetrics. With 149 Plates and Woodcuts. 4to. Philadelphia, 1864. £3.

Isherwood, —, Engineer-in-Chief, United States Navy.—Experimental Researches in Steam Engineering. Vol. I. 4to. 1863. £2 2s.

Jay (J. C.)—A Catalogue of the Shells arranged according to the Lamarkian System, with their Authorities, Synonyms, and references to Works where figured or described. 4th Edition. 4to. with Supplement. New York, 1852. 14s.

Johnson (W.)—On the Correlation, Conversion, or Allotropism of the Physical and Vital Forces. 8vo. Melbourne, 1864. 2s. 6d.

La Roche.—Pneumonia: its Supposed Connection, Pathological and Etiological, with Autumnal Fevers. Philadelphia. 12s. 6d.

La Roche.—Yellow Fever, considered in its Historical, Pathological, and Therapeutical Relations. 2 vols. 8vo. £1 10s.

Lawson.—Practical Treatise on Phthisis Pulmonalis; Pathology, Causes, Symptoms, and Treatment. 8vo. Cincinnati, 1861. £1 1s.

Lehmann.—Physiological Chemistry. Complete in 2 vols. Plates. Phila. £1 5s.

Malgaigne.—Treatise on Fractures. With 106 Illustrations. Philadelphia, 1859. 17s. 6d.

Maury, Nott, and Gliddon.—Indigenous Races of the Earth; or, New Chapters of Ethnological Inquiry. Coloured Plates and Woodcuts. Royal 8vo. Phila. £1 1s.

McCrady (J.)—Gymnopthalmata of Charleston Harbour. 8vo. 5 Plates. 1857. 5s.

Meigs (C.)—Treatise on Acute and Chronic Diseases of the Neck of the Uterus. 8vo. with 22 coloured Plates. Phila. £1 2s.

Meigs (C.)—Obstetrics; the Science and Art. 8vo. 121 Woodcuts. Phila. 17s.

Meigs (C.)—Woman; her Diseases and Remedies. 4th Edition, 8vo. Phila. 17s.

Meigs (C.)—A Practical Treatise on the Diseases of Children. 8vo. Phila. 18s.

Mitchell, Morehouse, and Keen. — Gunshot Wounds and other Injuries of the Nerves. 12mo. Philadelphia, 1864. 6s. 6d.

Morel.—Compendium of Human Histology. Illustrated with 28 Plates. Edited by W. H. Van Buren, M.D. 8vo. New York, 1861. 12s.

Morland (W.)—Diseases of the Urinary Organs; a Compendium of their Diagnosis, Pathology, and Treatment. 8vo. with Illustrations. 1858. 15s.

Morris.—An Essay on the Pathology and Therapeutics of Scarlet Fever. Philadelphia, 1858. Royal 8vo. 6s.

Natural History of the State of New York. 21 vols. 4to. Albany, 1849 to 1861.

Part 1. Zoology. By J. De Kay. 5 vols.

Part 2. Botany. By J. Torrey. 2 vols.

Part 3. Mineralogy. By Beck. 1 vol.

Part 4. Geology. By Mather, Emmons, Vanuxem, and Hall. 4 vols.

Part 5. Agriculture. 5 vols.

Part 6. Palæontology. By Hall. 4 vols.

Neumayer (G.)—Results of the Meteorological Observations taken in the Colony of Victoria in 1859-62, and of the Nautical Observations. 4to. With Charts. Melbourne, 1864. £3 3s.

Noeggerath and Jacobi.—(*See* page 4.)

Nott and Gliddon.—Types of Mankind. Royal 8vo. Plates. £1 1s.

O'Reilly (J.)—The Nervous and Vascular Connection between the Mother and Fœtus in Utero. 8vo. New York, 1864. 3s. 6d.

Otto.—A Manual of the Detection of Poisons by Medico-Chemical Analysis. 12mo. New York, 1857. 6s.

Overman.—A Treatise on Metallurgy, comprising Mining, and General and Particular Metallurgy. With 377 Illustrations. 8vo. New York. £1 10s.

Owen. — Geological Reconnaissance of Arkansas, made during 1857–60. 2 vols. 8vo. Illustrated. £1 10s.

Owen.—Geological Survey in Kentucky, made during 1854-59. 4 vols. 4to. and Plates. Very scarce. £6 6s.

Owen.—Geological Survey of Wisconsin and Minnesota. 2 vols. 4to. Plates. £2 2s.

Parrish.—A Treatise on Pharmacy, designed as a Text-Book for the Student, and as a Guide for the Physician and Pharmaceutist. 3rd Edition, 8vo. Philadelphia. £1 1s.

Regnault.—Elements of Chemistry. 2 vols. 1853. £1 10s.

Reid (David Boswell).—Quarterly Clinical Reports on Surgery. No. 1. Geelong, 1860. 2s. 6d.

Reports of Explorations and Surveys for a Railroad from the Mississippi River to the Pacific Ocean. 12 vols. in 13. 4to. with numerous Plates of Birds, Mammals, Reptiles, Plants, Shells, and Fossils. 1855-1860.

Report upon the Colorado River, explored in 1857–58. By J. C. Ives and A. Humphreys. 4to. with numerous Maps, Views, and Geological Plates. 1860. £1.

Report exhibiting the Experience of the Mutual Life Insurance Company of New York. 4to. half morocco. 1859. 12s. 6d.

Richardson.—Practical Treatise on Mechanical Dentistry. 8vo. with 110 Illustrations. Philadelphia, 1860. 14s.

Rokitansky.—Manual of Pathological Anatomy. 4 vols. in 2. 8vo. Philadelphia, 1855. £1 4s.

Say.—The Complete Writings of Thomas Say, on the Entomology of North America.

Say.—Conchology of the United States. Edited by W. G. Binney. (*See* page 6.)

Scanzoni.—Diseases of Females. 8vo. New York, 1861. 17s. 6d.

Schoolcraft.—The History, Condition, and Prospects of the Indian Tribes of the United States. Illustrated by Eastman. 6 vols. 4to. Plates. 1853–56.

Smith (Stephen).—Handbook of Surgical Operations, with 257 Figures. 12mo. New York, 1865. 8s.

Smithsonian Contributions to Knowledge. Vols. I.—V. 4to. with Maps and Plates. Washington, 1848–55. £5.

Stille.—Therapeutics and Materia Medica. 2 vols. 8vo. Philadelphia, 1860. £2 2s.

Storer.—A Dictionary of Solubilities. 8vo. Cambridge, Massachusetts. £1 5s.

Sullivant.—Contributions to the Bryology and Hepaticology of North America. 4to. 4s. 6d.

The New World in 1859; being the United States and Canada. Illustrated and described in Five Parts.—Part I. The United States. II. Scenes and Scenery. III. Upper and Lower Canada. IV. Things as they Are in 1859. V. Emigration, Land, and Agriculture, together with Routes of Travel, Fares, Distances, &c. With upwards of 180 Engravings, showing the Rivers, Lakes, and Mountains. 8vo. cloth. 8s.

Thomas.—A Comprehensive Medical Dictionary. Post 8vo. Philadelphia, 1864. 15s.

Transactions of the Medical Society of the State of New York. 8vo. 1832 to 1860; and 1 vol. of Addresses, 1817 to 1831, in all 20 vols. half-bound in 11. Albany, 1833–61. £8 8s.

Transactions of the American Medical Association. Vols. I.—XIII. 8vo. with Plates. Philadelphia.

Tryon.—Synonymy of the species of Strepomatidæ (Melanians) of the United States; with descriptions of Land, Fresh Water, and Marine *Mollusca*. 8vo. New York. 8s.

*** *See* American Journal of Conchology.

Tryon.—List of American Writers on Recent Conchology, with the Titles of their Memoirs, and Dates of Publication. 8vo. New York, 1861. 5s.

Tuomey and Holmes.—The Post-Pleiocene Fossils of South Carolina. 4to. Text and Plates. Charleston, 1858. £4 4s.

Tuomey and Holmes.—Fossils of South Carolina. 4to. Text and Plates. Charleston, 1856. £6 6s.

United States Pharmacopœia; Fourth Decennial Revision. 12mo. 1864. 6s.

Victorian Gazetteer and Road Guide, containing the most Recent and Accurate Information as to every Place in the Colony; with a Map. Compiled by Robt. Whitworth. 8vo. Melbourne, 1865. £1 1s.

Wood and Bache.—The Dispensatory of the United States of America. 12th Edition. 8vo. Philadelphia, 1865. £1 16s.

Wood.—Therapeutics and Pharmocology, or Materia Medica. 2 vols. 8vo. Philadelphia, 1857. £2.

Wood.—Treatise on the Practice of Medicine. 4th Edition. 2 vols. 8vo. Philadelphia, 1855. £2.

Woodward.—Outlines of the Camp Diseases of the U. S. A. 8vo. 1863. 10s.

Wynne (J.)—Report on the Vital Statistics of the United States. 1 vol. 4to. (not printed for sale). New York, 1857. £2 10s.

Wynne.—Private Libraries of New York. 8vo. New York, 1860. £1.

BIBLIOTHÈQUE DE PHILOSOPHIE CONTEMPORAINE

Volumes in-18 à 2s.

Ouvrages parus.

H. TAINE . . .	Le Positivisme anglais, étude sur Stuart Mill.
H. TAINE . . .	L'Idéalisme anglais, étude sur Carlyle.
PAUL JANET . . .	Le Matérialisme contemporain. Examen du système du docteur Büchner.
ODYSSE-BAROT . .	Philosophie de l'histoire.
ALAUX	La philosophie de M. Cousin.
AD. FRANCK . . .	Philosophie du droit pénal.
AD. FRANCK . . .	Philosophie du droit ecclésiastique : des rapports de la religion et de l'État.
ÉMILE SAISSET . .	L'Ame et la vie, suivi d'une étude sur l'Esthétique française.
ÉMILE SAISSET . .	Critique et histoire de la philosophie (fragments et discours).
CHARLES LEVÊQUE .	Le Spiritualisme dans l'art.
AUGUSTE LAUGEL .	Les Problèms de la nature.
CHALLEMEL LACOUR .	La Philosophie individualiste, étude sur Guillaume de Humboldt.
CHARLES DE RÉMUSAT	Philosophie religieuse.
ALBERT LEMOINE .	Le Vitalisme et l'animisme de Stahl.
MILSAND	L'Esthétique anglaise, étude sur John Ruskin.
A. VÉRA	Essais de philosophie hégelienne.
BEAUSSIRE . . .	Origines françaises du panthéisme allemand.
BOST	Le Protestantisme libéral.

FRENCH

SCIENTIFIC PUBLICATIONS.

REDUCTION IN THE PRICE OF FRENCH BOOKS.

Mr. BAILLIÈRE will be happy to execute orders for French Books at **10d.** to the **Franc** nett Cash.

Abeille.—Traité des Maladies à Urines Albumineuses et Sucrées. 1863. 8vo., avec une planche et figures. 6s. 6d.

Anger (B.)—Traité Iconographique des Maladies Chirurgicales. Précédé d'une Introduction par M. Velpeau. Première Monographie. *Luxations et Fractures.* Avec 8 planches coloriées. 4to. Livr. 1, 2, 3. Paris 1865. Each 10s.

Annales d'Hygiène Publique et de Médicine. Première série, collection complète (1829 à 1853), dont il ne reste que peu d'exemplaires, 50 vols. in-8, avec figures et planches et tables alphabétiques des 50 vols. £15. La 2e série commence avec 1854 à 1865. Prix de chaque année £1 4s.

Axenfeld—Des Névroses. Fol. 1864. 6s.

Barth et Roger.—Traité Pratique d'Auscultation. 7e édit. 18mo. 1865. 5s. 6d.

Bazin.—Leçons sur la Scrofule. 8vo. 2e édit. 1861. 6s. 6d.

Bazin.—Leçons Théoriques et Cliniques sur les Affections Cutanées Parasitaires. 2e édit. 8vo., orné de 5 pl. 1862. 4s.

Bazin.—Leçons Théoriques et Cliniques sur les Syphilides. 1859. 8vo. 3s. 6d.

Bazin.—Leçons Théoriques et Cliniques sur les Affections Cutanées de Nature Arthritique et Dartreuse. 1860. 8vo. 4s.

Bazin.—Leçons Théoriques et Cliniques sur les Affections Cutanées Artificielles et sur la Lèpre, les Diathèses, le Purpura, les Difformités de la Peau etc. 1862. 8vo. 5s.

Bazin.—Leçons sur les Affections Génériques de la Peau. 1862. 8vo. 4s.

Beclard.—Éléments d'Anatomie Générale. 4e édit. 8vo. 1865. 8s. 6d.

Beclard.—Traité Élémentaire de Physiologie. 5e édit. 8vo. 1865. 12s. 6d.

Belot (C.)—La Fièvre Jaune à la Havane, sa Nature et Traitement. 8vo. 1865. 3s.

Beraud (B. J.)—Atlas Complet d'Anatomie Chirurgicale Topographique, pouvant servir de complément à tous les ouvrages d'anatomie chirurgicale, composé d'environ 100 planches représentant plus de 200 figures dessinées d'après nature, par M. Bion. Figures noires, £2. 10s. Col. £5.

Bernard (C.)—Introduction a l'Étude de la Médecine Expérimentale. 8vo. Paris, 1865. 6s.

Bernard (Cl.)—Leçons sur les Propriétés des Tissus Vivants. 8vo., illustré. 1865. 6s. 6d.

Bossu.—Nouveau Compendium Médical à l'usage des Médecins-praticiens. 1862. 3e édit. 18mo. 6s.

Bouchardat.—Manuel de Matière Médicale, de Thérapeutique Comparée et de Pharmacie. 1864. 2 vol. 18mo. 4e édit. 12s.

Bouchardat.—Le Travail, son Influence sur la Santé. 1863. 1 vol. 18mo. 2s.

Bourguignon et Sandras.—Traité Pratique des Maladies Nerveuses. 2e édit. 1860–1863. 2 vol. 8vo. 10s.

Briand et Chaudé.—Manuel Complet de Médecine Légale, et contenant un Traité de Chimie Légale, par H. GAULTIER DE CLAUBRY. 7e édit. 1864. 8vo., avec 3 pl. gravées et 64 fig. 10s.

Brierre de Boismont.—Des Hallucinations. 8vo. 3e édit. Paris, 1862. 6s.

Brierre de Boismont.—Du Suicide et de la Folie Suicide. 2e édit. Paris, 1864. 6s.

Casper.—Traité Pratique de Médicine Légale, traduit de l'allemand sous les yeux de l'auteur, par M. Gustave Germer Baillière. 1862. 2 vol. 8vo. 12s.

Atlas colorié se vendant séparément 10s.

Chauffard.—Principes de Pathologie Générale. 8vo. Paris, 1862. 7s. 6d.

Charpentier.—Des Accidents Fébriles qui surviennent chez les Nouvelles Accouchées. 8vo. Paris, 1863. 3s.

Chenu.—Manuel de Conchyliologie et de Paléontologie Conchylio¹o⁊que. 1862. 2 vol. 4to., avec 4943 figures dans le texte, dont les principales coloriées. £1 7s.

Churchill (J. F.)—De la Cause Immédiate de la Phthisie Pulmonaire et des Maladies Tuberculeuses et de leur Traitement spécifique par les Hypophosphites. 2e édit. Paris, 1864. 8vo. 15s.

Clemenceau.—De la Génération des Éléments Anatomiques. 8vo. Paris, 1865. 3s. 6d.

Comte (A.)—Cours de Philosophie Positive. 2e édit. Revue par E. Littré. 6 vols. 8vo. Paris, 1864. £1 17s. 6d.

Cruveilhier.—Traité d'Anatomie Descriptive. Vol. 1, 8vo. 1865. 12s. 6d.

Cruveilhier.—Traité d'Anatomie Pathologique Générale. Vol. v. 8vo. *Completing the Work.* Paris, 1864. 6s.

Cullerier.—Précis Iconographique des Maladies Vénériennes. Liv. 1 à 8. 18mo. Paris, 1861-5. Chaque livraison 4s. 6d.

Davaine.—Traité des Entozoaires et des Maladies Vermineuses de l'Homme et des Animaux Domestiques. 1860. 8vo., avec 88 fig. 10s.

Deshayes.—Description des Animaux sans Vertèbres découverts dans le Bassin de Paris. 4to., avec planches. *48 livr. parus.* Paris, 1863–5. Chaque 5s.

Dictionnaire Encyclopédique des Sciences Médicales. Publié sous la Direction par MM. Raige-Delorme et A. Dechambre. *L'ouvrage sera publié en 25 vols. 8vo. avec fig. 8 vols. sont en vente.* Chaque vol. 10s.

Dictionnaire de Médicine, de Chirurgie, de Pharmacie, des Sciences Accessoires et de l'Art Vétérinaire. Par Nysten. 12e édit. par Littré. Grand 8vo. demi-rel. Paris, 1865. £1.

Dictionnaire (Nouveau) de Médicine, et de Chirurgie Pratique, illustré de figures intercalées dans le texte, *par une Société de Médecins et Chirurgiens de Paris.* Publié en 15 vols. Paris, 1865. L'ouvrage paraît par vol. tous les *trois mois.* 8 vols. sont en vente. Chaque 8s. 6d.

Donders.—L'Astigmatisme et les Verres Cylindriques. 1862. 8vo. 4s.

Edwards (Milne.)—Leçons de Physiologie et d'Anatomie comparée de l'Homme et des Animaux. 8 vols. 8vo. Paris. £3.
L'ouvrage aura 10 vols.

Eliphas (Levi).—Dogme et Rituel de la haute Magie. 1861. 2e édit. 2 vol. 8vo., avec 24 fig. 15s.

Eliphas (Levi).—Histoire de la Magie. 1860. 1 vol. 8vo., avec 90 fig. 10s.

Eliphas (Levi).—La Clef des Grands Mystères. 1861. 1 vol. 8vo., avec 22 pl. 10s.

Eliphas (Levi). — Philosophie Occulte. Fables et Symboles. 8vo. 1863. 6s.

Eliphas (Levi).—Science des Esprits. 8vo. 1865. 6s.

Falret.—Des Maladies Mentales et des Asiles d'Aliénés. Leçons Cliniques et Considérations Générales. 8vo. Paris, 1864. 12s.

Follin.—Leçons sur les Principales Méthodes d'Exploration de l'Œil Malade et en principal sur l'Application de l'Ophthalmoscope. 8vo., illustrated. 1863. 6s.

Frerichs.—Traité Pratique des Maladies du Foie. 1862. 8vo., avec 80 fig. 9s.

Garnier.—Dictionnaire Annuel des Progrès des Sciences et Institutions Médicales. 12mo. Paris, 1865. 4s.

Goldfuss (A.)—Petrifacta Germaniæ Iconibus et Descriptionibus Illustrata. 2e édit. 4to. Texte et Atlas de 199 planches, fol. Leips., 1862. £7 10s.

Gosselin.—Leçons sur les Hernies Abdominales faites à la Faculté. 8vo., fig. Paris, 1865. 6s.

Griesinger (W.)—Traité des Maladies Mentales Pathologique et Thérapeutique, traduit par Doumic. 8vo. Paris, 1865. 7s. 6d.

Grisolle.—Traité de Pathologie Interne. 9e édit. 1865. 2 vol. grand 8vo. 15s.

Grisolle.—Traité de la Pneumonie. 2e édit. 8vo. Paris, 1864. 7s. 6d.

Guardia.—La Médecine à travers les Siècles. *Histoire et Philosophie.* 8vo. Paris, 1865. 8s. 6d.

Guérin.—Leçons Cliniques sur les Maladies des Organes Génitaux Externes de la Femme 8vo. 1864. 6s.

Guersent.—Notices sur la Chirurgie des Enfants. 4 parts. 8vo. Paris, 1865. 4s.

Hardy.—Leçons sur les Maladies de la Peau. 4 vols. 8vo. Paris, 1863 à 1865. 16s.

Houel.—Manuel d'Anatomie Pathologique Générale et Appliquée. 2e edition. 1862. 18mo. 6s.

Hugueir (P. C.)—De l'Hystérométrie et du Cathéterisme Utérin. 8vo., avec 4 planches. Paris, 1865. 5s.

Husson.—Étude sur les Hôpitaux considérés sous le rapport de la construction, de la distribution de leurs bâtiments, de l'ameublement, de l'hygiène et du service des malades. Paris, 1868. 4to., avec 24 pl., tableaux et figures. £1.

Jaccoud.—Les Paraplégies et l'Ataxie du Mouvement. 8vo. Paris, 1865. 7s. 6d.

Jamain. — Nouveau Traité Élémentaire d'Anatomie Descriptive et de Préparations Anatomiques, suivi d'un Précis d'Embryologie, par M. Verneuil. 2e édition. 1861. 18mo., avec 200 fig. 10s.

Jamain.—Manuel de Petite Chirurgie. 1860. 3e édition. 1 vol. 18mo., avec 307 fig. 6s.

Jobert (de Lamballe.)—De la Réunion en Chirurgie. 8vo., avec 7 planches coloriées. Paris, 1864. 10s.

Lebert.—Traité d'Anatomie Pathologique Générale et Spéciale, ou Description et Iconographie Pathologique des Affections Morbides, tant liquides que solides, observées dans le corps humain. *Ouvrage complet.* Paris, 1855—1861. 2 vol. in-fol. de texte, et 2 vol. in-fol. comprenant 200 planches dessinées d'après nature, gravées et coloriées, £25.

Legouest.—Traité de Chirurgie d'Armée. 1863. 8vo., avec 128 figures. 10s.

Les Arts Somptuaires.—Histoire du Costume et de l'Ameublement, et des Arts et Industries qui s'y rattachent. 2 vol. de planches coloriées et 2 de texte, 4to. Demi-maroquin. Paris, 1858. £18 18s.

Lévy. — Traité d'Hygiène Publique et Privée. 4e édition. 1862. 2 vol. 8vo. 15s.

Liebreich (R.)—Atlas d'Ophthalmoscopie, représentant l'état normal et les modifications pathologiques du fond de l'œil visibles à l'ophthalmoscope; composé de 12 planches représentant 57 figures tirées en chromolithographie accompagnées d'un texte explicatif. In-folio. £2.

Luys.—Recherches sur le Système Nerveux Cérébro-spinal, sa Structure, ses Fonctions et ses Maladies. 8vo., avec atlas de 40 planches. 4to. Fig. noires £1 10s. Coloriées £3.

Maire.—Nouveou Guide des de Mères Famille. 8vo. 2nd édition. Paris, 1865. 4s.6d.

Malgaigne.—Manuel de Médecine Opératoire. 7e édition. 1861. 18mo. 6s.

Mandl.—Anatomie Microscopique. Paris, 1838-1857, *ouvrage complet.* 2 vols. in-folio, avec 92 planches. £13.

Martin et Collineau.—De la Coxalgie, de sa Nature, de son Traitement. 8vo., avec 30 fig. Paris, 1865. 6s.

Maunoury et Salmon.—Manuel de l'Art des Accouchements. 1861. 2e édition. 8vo. avec 32 fig. 6s.

Menière.—Les Consultations de Madame de Sévigné. 8vo. Paris, 1864. 2s. 6d.

Meunier.—La Science et les Savants en 1864-65. 2 vols. 12mo. Paris, 1865. 6s.

Niemayer.—Traitéde Pathologie Interne et de Thérapeutique. Vol. 1. 8vo. 1865. 7s. 6d.

Nysten.—Dictionnaire de Médecine, de Chirurgie, de Pharmacie, des Sciences accessoires et de l'Art Vétérinaire. 12e édition. Ouvrage contenant la synonymie grecque, latine, anglaise, allemande, italienne et espagnole, et le Glossaire de ces diverses langues. 1864. Grand 8vo., avec plus de 500 figures intercalées dans le texte. Demi-relié £1.

Peclet (E.)—Traité de la Chaleur considérée dans ses Applications. 3e édit on. Paris, 1860-61. 3 vol. grand 8vo. £1 16s.

Racle.—Traité de Diagnostic Médical, ou Guide Clinique pour l'Étude des Signes caractéristiques des Maladies. 3e édition. 1864. 1 vol. 18mo., avec 17 fig. 5s.

Requin.—Éléments de Pathologie Médicale. Vol. 5, 8vo.

Revue des Cours Littéraires.—Littérature. — Physiologie. — Théologie. — Eloquence.—Histoire.—Législation.— Esthétique.—Archéologie.

Revue des Cours Scientifiques.—Physique. —Chimie.—Botanique.—Zoologie.—Anatomie.— Physiologie. — Géologie.— Paléontologie.—Médecine.

Directeur, M. Eug. Yung; chef de la rédaction, M. Em. Alglave.

Ces deux journaux reproduisent les cours des Facultés de Paris, des départements et de l'étranger, et paraissent tous les samedis depuis le 5 décembre 1863. On peut s'abonner séparément à la partie littéraire ou à la partie scientifique.

Prix de chaque journal isolément, 15s. par an.; prix des deux journax réunis, 26s. par an.

Subscriptions commence on 1st December and 1st June.

Ricord.—Lettres sur la Syphilis. 3e édition. 18mo. 3s. 6d.

Robert.—Nouveau Traité sur les Maladies Vénériennes. 1861. 8vo. 7s. 6d.

Robin (Ch.)—Programme du Cours d'Histologie professe à la Faculté de Médecine. Paris, 1864. 4s.

Rollet.—Recherches Cliniques et Expérimentales sur la Syphilis. 1861. 1 vol. 8vo., avec atlas de 20 figures, dont 10 coloriées. 12s.

Rollet (F.)—Traité des Maladies Vénériennes. Vol. 1. 8vo. Paris, 1865. 6s. 6d.

Rose (H.)—Traité Complet de Chimie Analytique; édition française originale. Paris, 1859-1862. 2 vol. grand 8vo. £1.

Saurel.—Traité de Chirurgie Navale, suivi d'un Résumé de leçons sur le Service Chirurgical de la Flotte, par le docteur J. Rochard. Paris, 1861. 8vo., avec 106 fig. 6s. 6d.

Schweigger.—Leçons d'Ophthalmoscopie. 8vo., avec 3 planches, 8vo. Paris, 1865. 3s.

Sichel.—Iconographie Opthalmologique, ou Description avec Figures coloriées des Maladies de l'Organe de la Vue. 1852-1859. 2 vol. grand in-4, dont 1 volume de texte, et 1 volume de 80 planches coloriées. Rel. £9 10s.

Sous (G.)—Manuel d'Ophthalmoscopie. 8vo., avec figures. Paris, 1865. 3s. 6d.

Tardieu.—Manuel de Pathologie et de Clinique Médicale. 3e édition. 1864. 18mo. 6s.

Tardieu.—Dictionnaire d'Hygiène Publique et de Salubrité. 2e édition. 1862. 4 vol. gr. 8vo. £1 7s.

Thomas.—Éléments d'Ostéologie. Descriptive et Comparée de l'Homme et des Animaux Domestiques. 8vo., et avec Atlas de 12 planches. Paris, 1865. 10s.

Topinard (P.)—De l'Ataxie Locomotrice. 8vo. Paris, 1864. 6s. 6d.

Trousseau.—Clinique Médicale de l'Hôtel-Dieu de Paris. *Deuxieme édition*, corrigée et augmentée. Paris, 1864. 3 vol. 8vo. £1 5s.

Vernois.—Traité Pratique d'Hygiène Industrielle et Administrative, comprenant l'étude des établissements insalubres, dangereux et incommodes. Paris, 1860. 2 vol. 8vo. 13s. 6d.

Virchow.—Traité des Tumeurs. 2 vol. 8vo., avec fig. Sous presse.

Voisin (A.)—De l'État Mental dans l'Æcoolisme Aigu et Chronique et dans l'Absinthisme. 8vo. Paris, 1864. 2s. 6d.

Wecker.—Traité Pratique des Maladies des Yeux. Vol. 1. 8vo., avec 6 planches. Paris, 1865. 10s.

Watelot (A.)—Description des Plantes Fossiles du Bassin de Paris. 4to., avec planches. Livraisons 1 et 2. Prix de chaque 5s.

Wurts.—Traité Élémentaire de Chimie Médicale *Organique et Inorganique*. 2 vols. 8vo. 13s. 6d.

Just published, price 10s. 6d.

A PRACTICAL TREATISE ON COAL, PETROLEUM, AND OTHER DISTILLED OILS.

By Abraham Gesner, M.D., F.G.S.

Second Edition, Revised and Enlarged. By George Weltden Gesner, Consulting Chemist and Engineer.

THE ANATOMY OF THE EXTERNAL FORM OF THE HORSE.

With Explanations by James I. Lupton, M.R.C.V.S.

The Plates by Bagg and Stanton. Part I. containing 9 Plates and Explanations. Large Folio. Price, plain, £1 11s. 6d.; on India Paper, £2 5s. Part II., with 4 Plates (2 of which, the Leg and Mouth, are coloured). Plates Plain, 14s; coloured, £1.

*** The last Part of this important work will be published soon with the 8vo. vol. of Text, giving the Study of the External Form of the Horse, and the Physiology of Locomotion.

LIBRARY OF ILLUSTRATED

STANDARD SCIENTIFIC WORKS.

The following Volumes are now published:

MULLER'S PRINCIPLES of PHYSICS and METEOROLOGY. With 530 Woodcuts and Two Coloured Engravings. 8vo. 18s.

WEISBACH'S MECHANICS of MACHINERY and ENGINEERING. 2 vols. 8vo. With 900 Woodcuts. £1 19s.

KNAPP, RONALDS, RICHARDSON, and HENRY WATTS' CHEMICAL TECHNOLOGY; or, Chemistry in its Application to the Arts and Manufactures.

Vol. I., Parts 1 and 2, 8vo. contains—FUEL and its APPLICATIONS. Profusely Illustrated with 433 Engravings and 4 Plates. £1 16s.

Vol. I., Parts 3 and 4, in 2 vols. 8vo., contain—The ALKALIES and ACIDS. With numerous Illustrations on Wood. 1863. £2 14s.

These 2 vols. are entirely by Messrs. Richardson and Watts.

PART V. IN THE PRESS.

Vol. II., 8vo. contains—GLASS, ALUM, POTTERIES, CEMENTS, GYPSUM, &c. With numerous Illustrations. £1 1s.

Vol. III., 8vo. contains—FOOD GENERALLY: BREAD, CHEESE, TEA, COFFEE, TOBACCO, MILK, SUGAR. With numerous Illustrations and Coloured Plates. £1 2s.

QUEKETT'S (JOHN) PRACTICAL TREATISE on the USE of the MICROSCOPE. Third Edition, with 11 Steel and numerous Wood Engravings. 8vo. £1 1s. Reduced to 12s. 6d.

FAU'S ANATOMY of the EXTERNAL FORMS of MAN. For Artists. Edited by R. KNOX, M.D. 8vo. and an Atlas of 28 Plates, 4to. Plain, £1 4s.; Coloured, £2 2s.

GRAHAM'S ELEMENTS of CHEMISTRY, including the APPLICATIONS of the SCIENCE in the ARTS. Second Edition, with numerous Woodcuts. 2 vols. 8vo. £2. Vol. II. separately. Edited by H. WATTS, Esq. £1.

NICHOL'S ARCHITECTURE of the HEAVENS. Ninth Edition. 8vo. with 23 Steel Plates and many Woodcuts. 1851. 16s.

MITCHELL'S (J.) MANUAL of PRACTICAL ASSAYING. For the Use of Metallurgists, Captains of Mines, and Assayers in General. Second Edition, much enlarged, with Illustrations, &c. 8vo. £1 1s.

BERKELEY'S (Rev. J.) INTRODUCTION to CRYPTOGAMIC BOTANY. Illustrated with numerous Wood Engravings. 8vo. 1857. £1.

ANATOMY of the EXTERNAL FORM of the HORSE. With Explanations by J. I. LUPTON, M.R.C.V.S., and Plates by BAGG and STANTON. This Work will be completed in Three Parts, consisting of 18 to 20 Plates, with Explanations, and One Volume of Octavo Text, giving the Study of the External Form of the Horse and the Physiology of Locomotion. Part I., with Nine Plates and Explanations. Large folio. Price, plain, £1 11s. 6d.; on India Paper, £2 5s. Part II. with Four Plates (Two of which, the *Leg* and *Mouth*, are coloured). Plain, 15s.; Coloured, £1.

*** The last Part of this important Work will be published in the course of 1863, with the volume (8vo.) of Text.

GANOT.—ELEMENTARY TREATISE ON PHYSICS, EXPERIMENTAL AND APPLIED.

Translated on the Ninth Original Edition by Dr. Atkinson, of the Royal Military College, Sandhurst. With 600 Illustrations. Post 8vo. 1862. 12s. 6d.

(Adapted for the use of Colleges and Schools.)

Spottiswoode & Co., Printers, New-street Square, London.

47

This book should be returned to the Library on or before the last date stamped below.

A fine of five cents a day is incurred by retaining it beyond the specified time.

Please return promptly.

DUE OCT 22 1918

OCT 14 1939

MAR 1 44

3 2044 079 963 849